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Auto-Ionization in Doubly Excited Helium and the λ320.4 and λ357.5 Lines

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The probabilities of auto-ionization of the $2s^2\,{}^1S$, $2s2p\,{}^3P$, $2p^2\,{}^1D$, $3d^2\,{}^1G$ states of He are calculated with continuous wave functions which are obtained by numerical integration of the wave equation including the effect of exchange. The probabilities are 4×10^{14}, 5×10^{13}, 1×10^{14}, 4.9×10^{13} per second, respectively, for these states. On the basis of these calculations and the theoretical energies of the doubly excited states, the identification of the two lines λ320.4 and λ357.5 observed by Compton and Boyce and by Kruger is discussed. The former has been reasonably definitely ascribed to the transition $1s2p\,{}^3P-2p^2\,{}^3P$, the state $2p^2\,{}^3P$ not being subject to auto-ionization. The latter line cannot be satisfactorily accounted for with respect to both the position and the width of the line.

THERE have been many investigations on different aspects of the problem of doubly excited helium. Compton and Boyce,[1(a)] and later Kruger,[1(b)] observed in the extreme ultraviolet region two lines λ320.4 ($\nu=312{,}117$ cm^{-1}) and λ357.5 ($\nu=279{,}715$ cm^{-1}) which they ascribed to transitions from the doubly excited to the ordinary singly excited states of helium. Considerable interest on the energy states of doubly excited helium has been aroused by the suggestion, now abandoned, that the corona lines may be due to transitions among the doubly excited states of helium.[2] This has led to the theoretical calculation of these energy states by many authors.[3] Many attempts[4] have been made to observe the spectrum of doubly excited helium under experimental conditions that would have been most favorable for their excitation according to the theoretical excitation probabilities of these states by electron impact.[5] All these attempts have failed. Approximate calculations of the natural lifetime of the $2s3s^3S$ state as the result of auto-ionization have been carried out by Kreisler[6] and by Kiang, Ma, and Wu.[4] They found a natural lifetime of the order 10^{-14}–10^{-15} second.

It was pointed out by Kiang, Ma, and Wu that the failure to observe the spectrum of doubly excited helium may be understood on the basis of the theoretical great natural width of these states, since the spreading of a "line" over a spectral region of the order 100–1000 angstroms renders its observation exceedingly difficult. It was pointed out, however, by these authors that on accepting this theoretical probability of auto-ionization and on assuming the probabilities for

[1] (a) K. T. Compton, and Boyce, J. Frank. Inst. **205**, 497 (1928); (b) P. Gerald Kruger, Phys. Rev. **36**, 855 (1930).
[2] Rosenthal, Zeits. f. Astrophys. **1**, 115 (1932); Goudsmit and Wu, Astrophys. J. **80**, 154 (1934).
[3] F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 77 (1934); T. Y. Wu, *ibid.* **46**, 239 (1934); T. Y. Wu and S. T. Ma, *ibid.* **48**, 917 (1935); Chin, J. Chem. Soc. **4**, 344 (1936); W. Wilson, Phys. Rev. **48**, 536 (1935).
[4] Kiang, Ma, and Wu, Phys. Rev. **50**, 673 (1936); Chin. J. Phys. **2**, 117, (1936); F. Bundy, Phys. Rev. **52**, 452 (1937).
[5] Massey and Mohr, Proc. Camb. Phil. Soc. **31**, 604 (1935).
[6] Kreisler, Acta Physica Polonica **4**, 15 (1935).

TABLE I. Probabilities of auto-ionization.

State i	State f	Atomic wave functions	E_i in Rh	P in sec.$^{-1}$
$2s^2\,{}^1S$	$1sks\,{}^1S$	$\psi_{2s}\sim(1-\beta r)e^{-\beta r}$, $\beta=0.8469$	-1.4440	4×10^{14}
$2s2p\,{}^3P$	$1skp\,{}^3P$	$\psi_{2s}\sim(1-\beta r)e^{-\beta r}$, $\psi_{2p}\sim re^{-\gamma}$, $\beta=0.874$, $\gamma=0.862$	-1.5043	5×10^{13}
$2p^2\,{}^1D$	$1skd\,{}^1D$	$\psi_{2p}\sim re^{-\gamma r}$, $\gamma=0.815$	-1.328	1×10^{14}
$3d^2\,{}^1G$	$1skg\,{}^1G$	$\psi_{3d}\sim r^2e^{-\delta r}$, $\delta=0.659$	-0.868	4.2×10^{11}
$3d^2\,{}^1G$	$2skg\,{}^1G$	$\psi_{3d}\sim r^2e^{-\delta r}$, $\delta=0.659$	-0.868	4.9×10^{13}

the other doubly excited states to be of the same order of magnitude, one would expect a width of the order 1 angstrom for the lines λ320.4 and λ357.5 whereas the observed lines appear to be as sharp as the ordinary lines of He II. The situation is hence an unsatisfactory one. Either the calculated probability of auto-ionization for $2s3s^3S$ is grossly in error and the assumption that all the doubly excited states have about the same lifetime is not justified, or an explanation of the λ320.4 and λ357.5 lines must be sought elsewhere. The purpose of the present study is to make more calculations for a few doubly excited states of helium and to discuss the possible identification of the λ320.4 and λ357.5 lines.

PROBABILITY OF AUTO-IONIZATION

The general theory of the process of auto-ionization is a well-known one.[7] Let Ψ_i, Ψ_f be the wave functions of the initial (a doubly excited atom, for example) and the final (an ion plus an ejected electron) state. The probability of auto-ionization is then

$$P=\frac{4\pi^2}{h}|V_{if}|^2=\frac{4\pi^2}{h}\left|\int\Psi_i^*\left(\sum\frac{e^2}{r_{kj}}\right)\Psi_f d\tau\right|^2, \quad (1)$$

where the integration is taken over the coordinates of all the electrons. For a triplet or a singlet state, we have, respectively,

$$\Psi_i=\frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2)\mp\psi_b(1)\psi_a(2)), \quad (2)$$

$$\Psi_f=\frac{1}{\sqrt{2}}(\psi_c(1)\psi_k(2)\mp\psi_k(1)\psi_c(2)), \quad (3)$$

where ψ_a, ψ_b, ψ_c are the discrete atomic wave functions and ψ_k is the continuous wave function of the ejected electron. Kreisler employed for ψ_k the continuous wave function of hydrogen, thereby approximating the atomic field due to the nucleus and an electron by that of a bare nucleus of charge 1; whereas Kiang, Ma, and Wu employed, for $2s3s^3S$,

$$\psi_k=\frac{1}{h}\left(\frac{8\pi m}{k}\right)^{\frac{1}{2}}\frac{1}{r}\cos(kr-\alpha). \quad (4)$$

This amounts to employing for ψ_k its asymptotic form for large r which does not hold for small r, and with a phase α so chosen that (4) is not valid for large r. Both calculations neglected the effect of exchange on the solution ψ_k of the wave equation. As the value of the matrix element V_{if} in (1) depends rather strongly on the overlap of the various wave functions, it is thought that the insufficiently accurate ψ_k of the earlier calculations may cause considerable error in the probability of auto-ionization. In the present calculation we shall seek a solution ψ_k, taking into account the effect of exchange and the actual atomic field.

The function Ψ_f is the solution of the Schrödinger equation

$$\left[\Delta_1+\Delta_2+E+\frac{2Z}{r_1}+\frac{2Z}{r_2}-\frac{2}{r_{12}}\right]\Psi_f=0, \quad (5)$$

and ψ_c is the solution of

$$\left[\Delta+E_c+\frac{2Z}{r}\right]\psi_c=0, \quad (6)$$

where energy is in units of the ionization energy of hydrogen and distance in units of the first Bohr radius of hydrogen. Substitution of (3) into (5) and making use of (6) give the integro-differential equation[8]

$$[\Delta+k^2-V(r)](r\psi_{kl})=\mp U(r)(r\psi_c)\begin{cases}\text{triplet}\\ \text{singlet}\end{cases} \quad (7)$$

[7] Condon and Shortley, *Theory of Atomic Spectra* (1935), p. 369.

[8] Cf. P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

in which

$$V(r_2)=2\int\left(\frac{1}{r_{12}}-\frac{Z}{r_2}\right)\psi_c^2(r_1)d\tau_1 \qquad (8)$$

and

$$U(r_2)=2\int\frac{1}{r_{12}}\psi_c(r_1)\psi_{kl}(r_1)d\tau_1 - (k^2-E_c)\int\psi_c(r)\psi_{kl}(r)d\tau. \qquad (9)$$

k^2 is the kinetic energy of the ejected electron so that $E=E_c+k^2$. V is the energy of the ejected electron in the atomic field and $U(r)$ represents the effect of exchange. The subscript l is the azimuthal quantum number of the ejected electron. For a given initial state $\Psi_i(n_a, l_a; n_b, l_b)$ and a given $\psi_c(n_c, l_c)$, the value of l is determined by the following rule for the non-vanishment of the matrix element V_{if} and hence for the presence of auto-ionization: The states i and f must (*i*) be of the same parity, (*ii*) have the same value of J, and in the case of L, S coupling, (*iii*) have the same values of L and S. To obtain the solution of (7), since the effect of exchange is expected to be small, we shall, as an initial approximation, obtain the solution of the homogeneous equation

$$[\Delta+k^2-V(r)](r\psi_{kl})=0 \qquad (10)$$

by numerical integration. The solution ψ_{kl}^{0} so obtained is substituted into (9) and Eq. (7) is solved again by numerical integration. If the solution $\psi_{kl}^{(1)}$ so obtained differs considerably from the initial ψ_{kl}^{0}, Eq. (7) is solved again by using $\psi_{kl}^{(1)}$ in $U(r)$. The process is repeated until the ith solution $\psi_{kl}^{(i)}$ of (7) gives a value for V_{if} differing by less than 20 percent from the one obtained with the previous solution $\psi_{kl}^{(i-1)}$. It is found that the successive approximations oscillate about and converge upon the final solution very rapidly.

For the discrete wave functions, the simple variational wave functions of the earlier work[3] are employed. The continuous wave function is normalized according to (4) where $\cos(kr-\alpha)$ is the asymptotic form of $r\psi_{kl}$.

As an example, the equation for the radial part of the continuous wave function for the auto-ionization of $2s2p^3P$ is

$$\frac{d^2}{dr^2}(r\psi_{kl})+\left[2.4957+\frac{2}{r}+\left(4+\frac{2}{r}\right)e^{-4r}-\frac{2}{r^2}\right](r\psi_{kl}) = -\frac{64}{3}e^{-2r}r\left[\frac{1}{r^2}\int_0^r re^{-2r}(r\psi_{kl})rdr + r\int_r^\infty\frac{1}{r^2}e^{-2r}(r\psi_{kl})rdr\right].$$

The probabilities of auto-ionization of a few states of doubly excited helium calculated in this manner are given in Table I.

Concerning the magnitude of the probability of auto-ionization in general, very little can be said on the basis of these calculations. It appears, however, from the values of P for the auto-ionization of $3d^2\,{}^1G$ into $1s\times g\,{}^1G$ and $2s\times g\,{}^1G$ that P decreases very rapidly as the overlap of the atomic wave functions in the initial and the final states decreases.

THE λ320.4 AND λ357.5 LINES OF HELIUM

As the above calculations seem to indicate a probability of auto-ionization of the order 10^{13}–10^{14} per second for the doubly excited states of helium, and as the observed lines λ320.4 and λ357.5 do not seem to show any diffuseness, we would first try to identify them with transitions from such states as not being subject to auto-ionization. Of the configurations $2sns$, $2snd$, $2pnp$, $3dnd$, $2snp$, $2pnd$, only the states $2pnp\,{}^1P$, ${}^3P$; $2pnd\,{}^1D$, ${}^3D$; $3dnd\,{}^1D$, ${}^3D$ do not undergo auto-ionization. The energy of $2p^2\,{}^3P$ has been calculated by Wilson by the method of self-consistent field and is $E(2p^2\,{}^3P)=-1.4018$ Rh measured from the state of the naked nucleus.[3] This value is lower than that obtained by the use of simple variational wave functions, but a still better approximation to the true energy value of $2p^2\,{}^3P$ can be made by means of the method of Stevenson.[9] This method consists in using for the variational wave function the function $(1+c\cos\theta_{12})\Psi$ where Ψ is the correct combination of one-electron wave functions determined by the method of self-consistent field, and θ_{12} is the angle between r_1 and r_2 of the two electrons. Applica-

[9] A. F. Stevenson, Phys. Rev. **56**, 586 (1939).

tion of the variational principle to the determination of the parameter c leads to the secular equation for the energy of the system. For our purpose, we shall evaluate the integrals involved in the theory by means of the variational wave functions of Wu and Ma instead of Wilson's self-consistent field solutions. Since the energy correction given by Stevenson's method is small in any case, this procedure is completely justified.

Using the notation of Stevenson, and with $\psi_{2p}\sim re^{-\gamma r}$ where $\gamma=0.836$, we find

$$H_{01}=7\gamma/192,\quad H'_{11}=4\gamma^2/5,\quad \Delta E=-0.0091 \text{ Rh}.$$

Thus the corrected energy of $2p^2\,{}^3P$ is $-1.4018-0.0091=-1.4109$ Rh. With this value, the calculated frequency of the line $1s2p\,{}^3P-2p^2\,{}^3P$ is 313,348 cm^{-1} which differs by 0.4 percent from the observed 312,117 cm^{-1} for the line λ320.4. As the true value of $E(2p^2\,{}^3P)$ lies probably somewhat lower than -1.4109 Rh, one may feel reasonably sure of the identification of λ320.4 with the transition $1s2p\,{}^3P-2p^2\,{}^3P$.

With the other line λ357.5 ($\nu=179{,}715$ cm^{-1}), the situation is far less satisfactory. From the calculated energy states of doubly excited helium, it is found that only the lowest one, namely, $2s2p\,{}^3P$, lies within 280,000 cm^{-1} from the ionization limit of He I, the other states all being too high. On assuming the line λ357.5 to originate from $2s2s\,{}^3P$, it may then be compared with the following transitions

$$1s4s\,{}^3S-2s2p\,{}^3P=282{,}120 \text{ cm}^{-1};$$
$$1s4d\,{}^3D-2s2p\,{}^3P=280{,}968 \text{ cm}^{-1}.$$

But then the auto-ionization of $2s2p\,{}^3P$ would broaden the line to about 0.3A which is apparently too great compared with the observation. Also it is not clear why the transition $1s2s\,{}^3S-2s2p\,{}^3P$, which is expected to be stronger than the two above, did not appear on the same spectrogram. Hence it appears that, unless the calculated energies of the doubly excited states and the probabilities of auto-ionization are seriously in error, the line λ357.5 cannot be satisfactorily explained.

SATELLITE LINES IN C V AND C VI OBSERVED BY EDLÉN

Edlén and Tyrén observed groups of weak lines on the long wave-length side of the lines $1s^2\,{}^1S-1s2p\,{}^1P$, $1s^2S-2p^2P$ in C V and C VI, respectively.[10] These satellite lines they ascribed to $1s^22s^2S-1s2s2p^2P$, $1s^22p^2P-1s2p^2P$, ^2D, ^2S, etc., in C IV, and $1s2s^{1,3}S-2s2p^{1,3}P$, $1s2p^{1,3}P-2p2p^3P$, ^1D, ^1S in C V, respectively. An attempt has been made by the writer to correlate the individual satellite lines with such transitions on the basis of energies of such doubly excited states calculated by the variational method.[11] Most of these doubly excited states are capable of auto-ionization and accordingly the satellite lines should show some broadening. If, however, the probabilities of auto-ionization of such states as $1s2p^2\,{}^2D$ are of the same general order of magnitude as in He, namely, 10^{13}–10^{14} per second, the width of these lines in the region of 40A would be 0.001–0.01A, which is not hopelessly inconsistent with observation, in distinction to the case of the λ357.5 line of He.

[10] Edlén and Tyrén, Nature **143**, 940 (1939).
[11] T. Y. Wu, Phys. Rev. **58**, 1114 (1940).

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Further Studies on the Origin of Cosmic Rays

Helium Annihilation Rays and the Cause of Their Variability with Time

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We find definite evidence that a new band of rays which we interpret as helium annihilation rays does come in vertically at about the predicted latitude. We present a discussion of the possible composite character of the so-called silicon annihilation band and of the so-called oxygen annihilation band. We then bring forward an explanation of the cause of our large and already reported variability in the cosmic-ray intensities found in high altitude electroscope flights at Bismarck, Omaha, and Oklahoma City. We also make a new and more accurate determination of the value of the field sensitive and the non-field sensitive components of the incoming cosmic rays.

I. HISTORICAL SUMMARY OF THE DISCOVERY OF THE SILICON COSMIC-RAY BAND

IN our expedition to India in late 1939 and early 1940 we had found unambiguous evidence that in going from the magnetic equator near Bangalore north to Peshawar (Mag. Lat. 25° N) there was no change at all in the intensity of the vertically incoming cosmic rays between Bangalore and Agra (Mag. Lat. 17.3), but in going the next 7.7°, from Agra to Peshawar, there was a marked increase in that intensity, amounting to more than 20 percent.

We had gone to India primarily to look for just this cosmic-ray effect, for we had predicted on the basis of the hypothesis that the birth of the cosmic rays in interstellar space consists merely in the complete transformation into a "charged particle pair" (which we treat as an "electron pair"[1]) of the total rest-mass energy of the most abundant of the atoms found in interstellar space, namely, the atoms of silicon, oxygen, nitrogen, carbon, and helium.

If this were so we had computed from the Einstein equation $E=mc^2$ that each electron of the "electron pair" arising from such a transformation of the silicon atom (we have called these "silicon annihilation rays") would have an energy of 13.2 billion electron volts (Bev), not enough to break vertically through the earth's magnetic field at the magnetic equator in India, where we had computed that the requisite incoming charged particle energy was 17 billion electron volts, but it would have just about enough incoming energy to break through at somewhere near 20° N Magnetic Latitude, i.e., somewhere between Agra and Peshawar.

Having then found *experimentally* by balloon flights to very high altitudes a plateau of constant vertically incoming cosmic-ray energy between Bangalore and Agra and a new band of rays coming in between Agra and Peshawar, we provisionally identified this new band as the cosmic-ray silicon annihilation band.

We found additional evidence for the correctness of the foregoing interpretation in the fact that when in our high balloon flights we again sent up to the very top of the atmosphere in place of the pairs of counters (one parallel to the other and some six inches above it) either a recording *electroscope* or a *single counter*, both of these two latter receivers being of the kind that respond to rays coming in *from all directions* rather than merely to rays coming in vertically, then, instead of finding this plateau of constant cosmic-ray intensity between Bangalore and Agra succeeded by a sudden rise in intensity between Agra and Peshawar, we found both the electroscope and the single-counter readings rising continuously both between Bangalore and Agra and also between Agra and Peshawar.

[1] A mesotron pair is barred out by its short lifetime. The only choice is between an electron pair and a proton pair, but the difference between the latitude of entrance of electrons and protons entering the earth's magnetic field from this mode of origin is in no case, not even in the case of the He annihilation rays, large enough to be detected with the resolving power of the experimental techniques we have so far used. However, we hope to obtain a resolution which will differentiate between these alternatives. See footnote 4, Phys. Rev. **61**, 398 (1942). We miscalculated the difference in Phys. Rev. **63**, 245 (1943), so that the conclusion there reached is not yet a valid one.

This last behavior is just what is to be expected when the electroscope or the single counter is the measuring instrument. The reason for this difference can be seen from a glance at our discussion of the Lemaitre-Vallarta curves reproduced in one of our preceding papers.[2]

II. THE MORE PRECISE MEANING OF THE SILICON BAND

It is desirable to call attention to one further characteristic of this band of incoming cosmic rays that we have above and, in previous papers, designated simply as the silicon-band, namely, its possible composite character. Although, according to Bowen's measurements[3] Si (at. wt. 28.3) is probably ten times more abundant in interstellar space than are any of the three closely adjacent elements Al (at. wt. 27.1), P (at. wt. 31), and S (at. wt. 32) these are all so close to Si in weight that their annihilation rays would be quite inseparable by the type of tests we have so far made.

Hence, for simplicity we designated, and shall continue to designate, this observed band of incoming rays the "*silicon-band*" without wishing to deny to it the possibility of a composite structure. Indeed, P. Swings, who, with his collaborators, has recently made elaborate studies on the abundance of both atoms and molecules in interstellar space,[4] says, "It may safely be assumed that the atomic populations in interstellar space of H, O, N, and C per cm^3 are between 1 and 10^{-3}." These estimates of the actual interstellar abundance of these atoms are not out of harmony with Bowen's measurements of the relative-interstellar abundance of atoms. From these he finds[3] the He atom 1/10 as abundant as the H atom, and the atoms of C, N, O, and Si each of about one-tenth the abundance of the atom of He.

Swings also writes us "that the interstellar abundance of the carbon compound molecules CH and CH^+ must be of the order 10^{-6} per cm^3." In other words, the most abundant interstellar *molecules* would have only 1/10,000 of the abundance of the foregoing abundant atoms C, O, N, and Si, so that so far as the origin of the "field sensitive cosmic rays"[5] is concerned, *no molecules and no atoms heavier than the atoms causing the Si band need to be considered at all.* This introduces a very great simplification into the whole problem of origin.

III. THE 1940 PREDICTIONS OF COSMIC-RAY BANDS AND OF PLATEAUS OF CONSTANT COSMIC-RAY INTENSITIES

If, then, our hypothesis as to origin is correct, there can be four, and only four, cosmic-ray bands in addition to the Si band to look for, namely, the O, N, C, and He bands, which should have the energies required to enable them to begin to break vertically through the resistance of the earth's magnetic field at a series of four different latitudes as the observer goes north from the latitude of first entrance of the silicon band.

However, on account of the dissymmetry of the earth's magnetic field we had computed as early as 1939 that the silicon band (energy 13.2 Bev), though it could not get vertically through at the equator in India, where the required energy was 17 Bev) could get through at the equator off the coast of Peru where we computed that the requisite energy was but 13 Bev.

As soon, then, as we had found the silicon band in India we were able to predict, and in fact published the prediction, that there should be a very long plateau of constant vertically incoming cosmic-ray intensity extending from Mollendo, near the magnetic equator in Peru, clear up to the middle of Mexico (Mag. Lat. 32° to 34°) at which latitude the oxygen annihilation band should begin to come in and of course remain in at full strength for all more northerly latitudes.

But the oxygen band like the silicon band might have a bit of complexity about it for, according to Bowen's table,[3] the Ne atom has one-tenth the interstellar abundance of O. Be-

[2] See Fig. 2, R. A. Millikan, H. V. Neher, and W. H. Pickering, Phys. Rev. 61, 401 (1942).

[3] See R. A. Millikan, H. V. Neher, and W. H. Pickering, Phys. Rev. 61, 399 (1942), footnote 5.

[4] P. Swings, Astrophys. J. 95, 270 (1942). See also *ibid.* 92, 292 (1942), and Astronom. Soc. Pac. 54, 3 (1942), and J. Roy. Astronom. Soc. Canada 35, 75 (1941).

[5] We define non-field sensitive cosmic rays as those found at the magnetic equator in India when the measuring instrument that is carried to the top of the atmosphere is an electroscope. Field sensitive rays are the *additional* rays that come in when the electroscope measurements are carried out at successive latitudes between the equator and the pole.

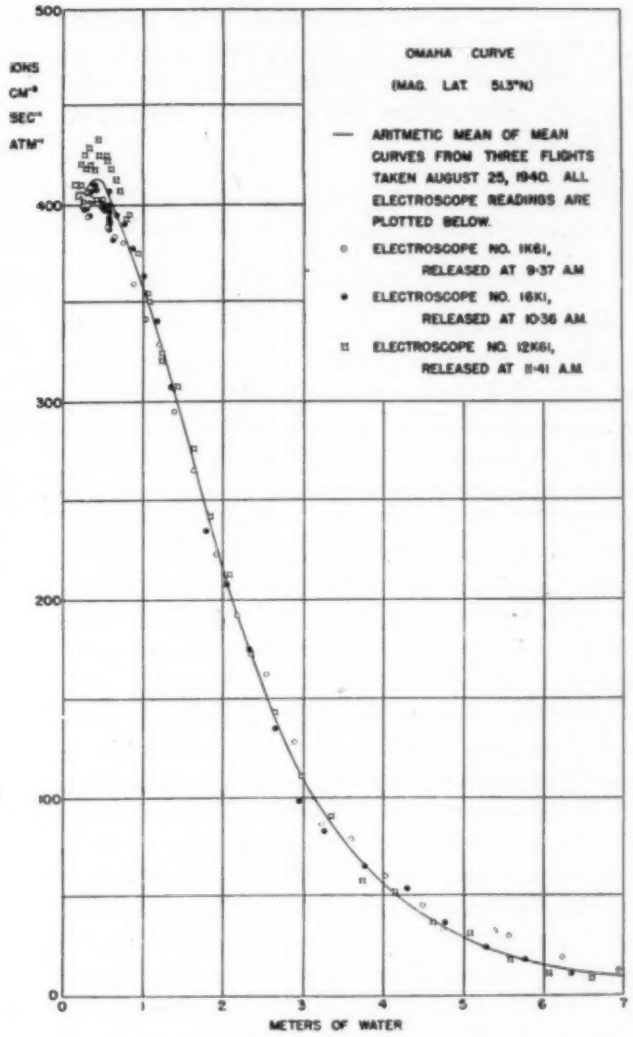

FIG. 1. Details showing consistency obtained in three successive flights in one day. Similar consistency was shown between the component curves making up each of the five mean curves of Fig. 2. All of these flights were made within a period of 13 days from August 21 to September 3, 1940.

cause of its weakness and closeness to O (atomic numbers 10 and 8, respectively) we had no hope of separating the two effects and decided to designate the whole effect as the "O annihilation band," as we had done with the similarly complex silicon band.

But because of the equality in the interstellar abundance of O and N at a latitude a very small number of degrees north of the first appearance of the O band, the N band should add its equal intensity to the total vertically incoming energy. We of course had little hope of separating these O and N bands, but we had confidence that the vertically incoming cosmic-ray intensity at Pasadena (Mag. Lat. 40.7° N) would represent the addition of the intensity of the O and N bands and would therefore be notably larger than that to be found at the first latitude at which the O band came in in its full strength.

Again, we predicted from our hypothesis that in going a *very* few degrees north of Pasadena there would be another increase in vertically incoming cosmic-ray intensity roughly equal to half the increase between Mag. Lat. 33° N and 40.7° N, which latter increase should be due to the joint effect of the O and N bands, for according to Bowen O, N, and C all had equal abundance.

We expected the most crucial test of this whole hypothesis to come in the testing of the prediction that between say Mag. Lat. 44° N and 54° N there should be found another flat plateau of constant vertically incoming cosmic-ray energy since there are no abundant atoms at all of weights between

those of C and He and we computed from Lemaitre and Vallarta's curves that the He atom-annihilation ray could not break vertically through the earth's magnetic field farther south than at about Mag. Lat. 54° N.

IV. REASONS FOR MAKING THE 1940 SERIES OF INCOMING COSMIC-RAY ENERGY MEASUREMENTS WITH ELECTROSCOPES AT A SERIES OF DIFFERENT LATITUDES

All the foregoing predictions had been made upon our return from India in the early spring of 1940. We knew, however, that we could not develop the necessary new equipment for putting these predictions to careful experimental test in less than a year's time. But we were already well supplied with excellent recording electroscopes such as we had used, in part, in India. Since, then, the total cosmic-ray energy coming into the atmosphere at any latitude, no matter from what direction, is an important measurement which could be made most accurately with electroscopes, since, further, a series of such measurements taken in a series of latitudes in such rapid succession as to reduce the likelihood of time-changes was a matter of considerable importance, and since this was the only accurate way of getting the ratio of the field sensitive to the non-field sensitive incoming rays, we decided to interrupt, in the summer of 1940 for a period of two weeks, the preparations for the above-mentioned vertical counter tests planned for the year 1941–1942, in order to make a series of flights with electroscopes in September, 1940.

The absorption of all three of us in war projects has delayed the working up and presentation of these data until the present.

Meantime, the crucial vertical counter tests of the above-mentioned series of predictions as to cosmic-ray bands and plateaus were carried out in December, 1941 and March and April, 1942, and have already been published[6] *with results which appear to confirm all of the predictions made.* However, we have not yet located with the aid of vertical counters the latitude of entrance of the vertically incident He annihilation rays. We hope to do this at the close of the war, but the present data, taken with electroscopes, throw some light on this point and on other points of importance, as indicated below.

This expedition, then, was undertaken in the summer of 1940 because (1) we had the equipment ready and could carry out these high flights with electroscopes to best advantage in the more stable weather conditions usually prevailing in the Middle West in late summer and early fall; (2) because we had already found in very high electroscopes flights in high magnetic latitudes (Omaha, Bismarck, Saskatoon) as yet unexplained variabilities with time[7] which were conspicuously absent in India[8] and which we thought might disappear in part, at least, if a series of flights at different latitudes was taken all in one season and in as rapid succession as possible; (3) because such a series of more accurate electroscope flights would establish with greater certainty the relation between the field sensitive and the non-field sensitive portions of the incoming cosmic rays such as had been thus far defined only in terms of the total integrated value of the ionization found at a given latitude through ionization measurements made with electroscopes or single counters as they are carried from the lowest point at which cosmic-ray ionization can be detected up to the top of the atmosphere; (4) because on account of the shape of the Lemaitre-Vallarta curves in high magnetic latitudes there was a possibility of throwing some light, even with electroscope flights, on the reality, and latitude of entrance, of the helium annihilation band.

V. THE NEW MEASUREMENTS

At Bismarck, North Dakota three flights were made on the same day, August 21, 1940, the first pair of balloons used for carrying up the recording electroscope being released at 8:45 A.M., the second at 9:50 A.M., the third at 1:46 P.M. Four days later, namely, on August 25, 1940, three more similar flights were made at Omaha, the first ascent starting at 9:37 A.M., the second at 10:36 A.M., the third at 11:41 A.M. This process was repeated at Oklahoma City on

[6] R. A. Millikan, H. V. Neher, and W. H. Pickering, Phys. Rev. **63**, 234–245 (1943).

[7] See R. A. Millikan, H. V. Neher, and W. H. Pickering, Phys. Rev. **61**, 405–406 (1942).

[8] See R. A. Millikan, H. V. Neher, and W. H. Pickering, Phys. Rev. **61**, 408 (1942), and especially Fig. 1 on page 408.

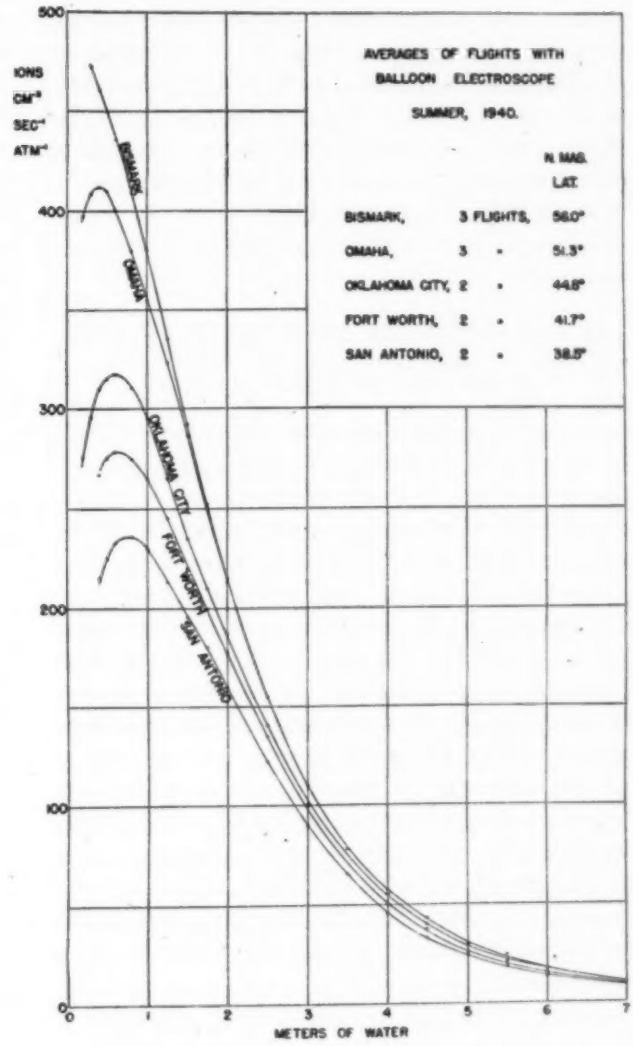

FIG. 2. Soft He rays make Bismarck-Omaha difference only at high altitudes; penetrating carbon rays cause difference, extending down to low altitudes, between Oklahoma City and Omaha curves.

August 29, at Fort Worth on September 2 with two flights, and at San Antonio on September 3 with two flights. All of these flights, then, were taken within a period of thirteen days, during which the atmospheric conditions were particularly stable. The set of resulting curves, therefore, has a much better chance of being free from errors caused by possible changes with time in the incoming cosmic-ray intensities than have those we have previously published, some of which were taken some years apart. Furthermore, we have never taken a series of flights with different electroscopes that showed throughout as great a self-consistency in each given locality as do these.

Figure 1 shows just how we treated the data at Omaha, for example. It is altogether typical of the data taken in all five of the different latitudes.

In this figure every one of the readings of the photographic film for each of the three flights made at Omaha is recorded. Our procedure for getting the final mean curve for this locality from these readings was to draw separately the full curve of each flight; then to read off on each of these three curves the ionization at a given altitude, say the ionization corresponding to 2 meters of water beneath the top of the atmosphere; then to average these three readings at 2 meters; and having obtained this sort of an average at a whole series of chosen altitudes up to as near the top of the atmosphere as the readings extend, to draw through these averaged points the final curve. This is the full line shown

in Fig. 1. It is reproduced again in Fig. 2 along with the mean curves obtained in this way at all of the five indicated latitudes. The area underneath each of these curves is the total integral of the cosmic-ray energy entering the atmosphere at the latitude in question. It can be reduced to electron volts by multiplying by 31, the average number of electron-volts required to produce an ion in air.

VI. THE BEARING OF THESE CURVES ON THE REALITY, AND LATITUDE OF ENTRANCE, OF HELIUM ANNIHILATION RAYS

From as careful a study as we have been able to make of the Lemaitre-Vallarta curves reproduced in Fig. 2 of our earlier paper,[9] supplemented by a little adjustment, especially in the case of the O band because of our own observations shown in Fig. 4, page 403 of reference 9(a), and because of the evidence presented in pages 239 and 242 of reference 6, that off the west coast of South America the electronic energy necessary to get vertically through the resistance of the earth's magnetic field at the equator is 13 Bev instead of the 15 Bev assumed by Lemaitre and Vallarta (probably a correct assumption for computing incoming energies north of Pasadena), we have estimated in Table I the critical magnetic latitudes for the entry of the cosmic annihilation rays as measured by electroscopes.

The table brings to light the bad overlapping of the various bands and the impossibility of unscrambling them, *save in the case of the helium band*. But because of the wide difference in energy between helium and carbon, the former is able to appropriate to itself entirely all latitudes above 51°, so that on the basis of the atom-annihilation hypothesis, if in going north new cosmic rays come in between 51° and 59°, they can only be helium annihilation rays. In fact, as shown in Fig. 2 there can be no uncertainty about the appearance of a new band of rays between Omaha and Bismarck and a band so little penetrating, as helium rays should be, that it cannot throw its influence down even to the 2-meter level, after which depth the Bismarck curve is seen in Fig. 2 to coincide completely with the Omaha curve.

This is not at all so with the difference between the Omaha and the Oklahoma City curve because this difference is primarily due to the carbon band, for carbon rays have an energy of 5.6 Bev and this is sufficient to throw their influence down nearly to sea level. If, on the other hand, one assumed incoming cosmic-ray energy lying between the C and He bands, then the Oklahoma City curve would certainly be expected to run together with the Omaha curve at a much higher altitude than Fig. 2 shows to be the case.

We expect as soon as possible after the war to locate the latitude of entrance of the vertically incoming helium rays by the vertical counter technique, but the evidence here as to its existence and location is so good that we feel confident that this prediction will be verified as well as this has been done with the whole series of predictions discussed above.

VII. THE VARIABILITY IN INCOMING COSMIC-RAY INTENSITIES

We have published on several occasions in recent years the discovery of large and thus far wholly inexplicable changes in incoming cosmic-ray intensities as measured by the electroscope technique in the northern part of the United States.[10]

TABLE I. Critical magnetic latitudes in North America for entry of cosmic annihilation rays.

Atom	Energy	Latitude of first entry on western horizon	Latitude of full entry on eastern horizon	Latitude of vertical entry
He	1.88 Bev	~51°	~59°	~54°
C	5.6 Bev	~32°	~49°	~42°
N	6.6 Bev	~27°	~48°	~39.5°
O	7.5 Bev	~22°	~46°	~33.5°

Thus, between August 21 and September 3 of 1937 we made good flights with electroscopes at Omaha to such heights as to get definitely over the maximum of ionization in our electroscopes. The value of this ionization at the top when reduced to standard air density was 338 ions

[9] (a) Millikan, Neher, and Pickering, Phys. Rev. 61, 397 (1942). (b) See also Lemaitre and Vallarta's original papers in Phys. Rev. 49, 719 and 50, 503 (1936); also 43, 87 (1933).

[10] See R. A. Millikan and H. V. Neher, Phys. Rev. 56, 491 (1939).

per cm³. In 1938 we went purposely to Omaha in winter (December 22 and 23) and repeated these experiments and found a maximum ionization at the top of 364 ions, an increase of nearly 8 percent. Again, the maximum ionization shown at the top in the September 25, 1940 flights herewith reported (see Figs. 1 and 2) is 413 ions per cm³, an increase over December, 1938 of 13.4 percent.

TABLE II. Time changes in the earth's magnetic field. H in c.g.s. units.

	1915	Annual changes	1940
Bismarck	0.161	−0.00027	0.154
Omaha	.197	−.00049	.185
Oklahoma City	.241	−.00063	.225
St. George	.247	−.00037	.238
Mt. Wilson	.265	−.00035	.256

Magnetic records from Mount Wilson, California; Tucson, Arizona; Cheltenham, Maryland

1937	September	3	No storm
1938	July	10	No storm
	July	15	Small storm July 13 to 17
	December	22	*H* about 0.00030 lower than normal
1940	August, September		No storms.

Again, the maximum which we obtained in Bismarck in the summer of 1938 (July 5) was 374 ions/cm³, while the 1940 maximum found at Bismarck August 21 and reported in Fig. 2 was 485 ions/cm³, or an increase over 1938 of 29.7 percent.

Still further, our maximum obtained in Oklahoma City in mid July (11, 12, 13) of 1938 was 280 ions/cm³, while the maximum shown in summer of 1940, August 29 (see Fig. 2), is 319 ions/cm³, an increase over 1938 of 14 percent.

Contrast the foregoing findings with the following facts. We made electroscope flights at San Antonio in the summer of 1936 and got a maximum of 234 ions/cm³ and repeated these flights on September 3, 1940 and found (see Fig. 2) precisely the same maximum as in 1936, *viz.*, 234 ions/cm³. Also, not only was our maximum at Madras, India in 1936 the same as in February in 1940, but as shown in the report of our India work[11] the two curves taken four years apart are everywhere indistinguishable.

In a word, while the cosmic rays coming in at Madras and at San Antonio seem to remain amazingly constant, yet in the northern part of the United States they show amazing fluctuations.

We seek the explanation of this strange behavior in the atom-annihilation hypothesis as follows: We assume for simplicity that the cosmic processes creating the cosmic rays cause an essentially constant incidence of all the five cosmic-ray bands on the earth. According to Bowen, He is ten times more abundant than C, N, O, or Si, and even from the energy standpoint, if the probability of the transformation of the whole rest mass into an electron pair is the same for all atoms, the energy in the helium band is some 3.5 times that in the C, N, and O bands, and some 1½ times the energy of the Si band.

Bismarck and Omaha both lie close to the southern edge of the polar cap of He annihilation rays, which we have computed as located for vertical-counter measurements at 54° N Mag. Lat. and for electroscope measurements at between 51° N Mag. Lat. and 59° N Mag. Lat. With even slight changes in the earth's magnetism this edge of the He polar cap will move north or south and, since the resistance to incoming electrons is very small in northern latitudes, the relative effect of changes in the earth's magnetic field may be correspondingly large depending upon the kind of cause that makes the change. In equatorial latitudes, where the resistance to incoming electrons is say 8 times larger than at Bismarck or Omaha, the fluctuations in the earth's magnetic field will have smaller influence and *no influence at all unless the point of observation is near the edge of one of the five polar caps corresponding to the latitude of entrance of one of the cosmic-ray bands.*

TABLE III. Tucson values of H corresponding to the year and month at which the foregoing cosmic-ray measurements were made.

Omaha	Bismarck	Oklahoma City
Sept. 1-30, 1937, 26189γ Dec. 1-31, 1938, 26162γ Aug. 1-31, 1940, 26140γ	July 1-31, 1938, 26182γ Aug. 1-31, 1940, 26141γ	July 1-31, 1938, 26182γ Aug. 1-31, 1940, 26141γ

In the present experiments according to Table I the helium rays from the western horizon are already passing through the electroscope in the upper levels of the atmosphere and a very little change in the earth's magnetic field that would make the band move say 2° southward, according to Lemaitre-Vallarta curves, would throw the

[11] See H. V. Neher and W. H. Pickering, Fig. 1, Phys. Rev. 61, 408 (1942).

greater part of the helium band's energy into the top of the Omaha curve. *It is presumably actually there in these observations* in which the Omaha curve runs higher than we have observed it to do in any of our other trials there.

Oklahoma City is the only place, save Bismarck and Omaha, at which these changes have been observed, and here they were in smaller amount. Oklahoma City is actually quite close to the computed latitude of entrance of the carbon band. The reason for the high values of the Bismarck, Omaha, and Oklahoma City curves in 1940 is that then the edge of the He and C polar caps were farther south than at the time of previous readings. Furthermore, as Table I shows, the width of the slope of the rise to a new plateau increases greatly for the more southerly bands. This is another reason why a small change in the earth's magnetic field has little effect in the more southerly latitudes, but a large effect in the northerly ones.

According to this hypothesis, an increase in the intensity of the cosmic rays at Bismarck and Omaha means a southward movement of the edge of the helium polar cap and such a movement in turn means a weakening in the strength of the earth's magnetic field. Such a weakening is actually shown in Table II which has just been prepared by Dr. S. B. Nicholson of the Mount Wilson Observatory who is looking for correlations between sun-spot activity and magnetic storms, and who also tells us that magnetic storms in general correspond to a weakening rather than a strengthening in the earth's field. Further evidence of such weakening of the earth's field between May, 1936 and May, 1938 can be seen in Fig. 1,[12] which we took from the paper of S. E. Forbush,[13] of the Carnegie Institution of Washington.

[12] See R. A. Millikan and H. V. Neher, Phys. Rev. **56**, 492 (1939).
[13] S. E. Forbush, Phys. Rev. **54**, 975 (1938).

In further check on the foregoing apparent correspondence between cosmic-ray intensity and the strength of the earth's magnetic field in the western part of the United States, Director L. O. Colbert of the Coast Geodetic Survey has kindly furnished us with the data which we have put together in the form shown in Table III. This is more definite than Table II in indicating that at every one of the above observed times (year and month) in which we observed an increase in cosmic-ray intensity over its value at the same station at some other year and month there had also occurred a corresponding small decrease in the horizontal component H of the earth's magnetic field at the Tucson magnetic observatory.

VIII. THE FIELD SENSITIVE COMPONENT OF THE COSMIC RAYS

In view of the greater accuracy in these electroscope measurements than of our preceding ones, we have computed from the new curves of Fig. 2 combined with the unchanged measurements at Madras,[14] that *the field sensitive component defined through these electroscope readings is 65 percent of all incoming cosmic-ray energy*. All this is due to incoming charged particles, certainly electrons or protons. There is at present no way of finding what fraction of the non-field sensitive component is due to charged particles and what to photons, though part of it is unquestionably due to the former.

This investigation, like many preceding ones, has had support from the Carnegie Corporation of New York administered by the Carnegie Institution of Washington. For this aid, as well as for the aid given us by Dr. Seth B. Nicholson and Director Colbert, the authors wish to express their keen appreciation.

[14] See Figs. 1, 7, and 8 of Millikan, Neher, and Pickering, Phys. Rev. **61**, 397 (1942).

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The Forces Between a Hydrogen Molecule and a Hydrogen Atom

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The paper contains the results of calculations of (1) repulsive exchange forces, (2) attractive van der Waals forces between H_2 and H atoms. The method used is that developed in an earlier communication. Results for small distances of separation differ considerably from published data on interaction energies deduced from collision cross sections. Reasons for the discrepancy are discussed. Figures 1 and 2 represent potential energy curves for the region around the van der Waals minimum; they exhibit the asymmetry of the interaction.

I. THEORY

THE forces between H_2 molecules have been calculated with the use of a simple molecular wave function in a recent publication.[1,2] The method and many of the details there developed lend themselves readily to the calculation of the interaction between an atom and a molecule, a matter regarding which there is some experimental information.[3] In the present paper we present the significant points of the theory and the results, making use throughout of the notation of reference 1. The simplifications formerly made will again be used; in particular, a Heitler-London function with adjustable screening constant is chosen to represent the molecule. The atom will in this case be described by a function having the same screening constant as the molecule, a procedure which reduces the complexity of computations greatly without, it seems, falsifying the results in an essential way. To show the effect of the somewhat arbitrary choice of screening constant, the calculations are carried out for several values of this parameter. The preceding paper[1] will hereafter be referred to as I.

Let the nuclei of the three interacting atoms be localized at the points a, b, and c. These letters will also be used to denote the electronic orbital functions centered about these points. Thus, in the notation of I, three state functions describing the three-particle system can be formed for which the Z component of the total spin is zero:

$$\begin{aligned}\Psi_1&=|a\alpha \quad b\beta \quad c\alpha|,\\ \Psi_2&=|a\beta \quad b\alpha \quad c\alpha|,\\ \Psi_3&=|a\alpha \quad b\alpha \quad c\beta|.\end{aligned} \tag{1}$$

Of these, we can construct by known rules two doublet functions:

$$\psi_A=\sqrt{\tfrac{1}{2}}(\Psi_1-\Psi_2), \quad \psi_B=\sqrt{\tfrac{1}{2}}(\Psi_3-\Psi_2).$$

In general, the correct Ψ is a combination of these two, and the energy E is given by

$$\begin{vmatrix} H_{AA}-E\Delta_{AA} & H_{AB}-E\Delta_{AB} \\ H_{AB}-E\Delta_{AB} & H_{BB}-E\Delta_{BB} \end{vmatrix}=0.$$

We note, however, that ψ_A represents a bond between atoms a and b, ψ_B a bond between a and c. (The criterion for existence of a bond between two atoms is symmetry with respect to an interchange of the bonded nuclei.) If, then, we suppose that a and b form our molecule, we may limit our consideration to ψ_A alone. In this case, the determinantal equation reduces to

$$E=\frac{H_{AA}}{\Delta_{AA}}. \tag{2}$$

The functions a, b, c used in Eqs. (1) are all one-electron orbitals and hence include no ionic terms. At close distances of separation ionic states certainly make a contribution to the energy and, in an exact calculation, have the effect of lowering it. Even when the functions describing the atom and the molecule at infinite

[1] H. Margenau, Phys. Rev. **63**, 131 (1943).
[2] Meanwhile, an interesting paper by J. DeBoer, Physica **9**, 363 (1942), dealing with the same problem, has come to my attention. His final results, which do not differ greatly from ours, are obtained more simply and with much less labor by neglecting most of the exchange integrals, to the investigation of which reference 1 was chiefly devoted. As DeBoer admits and as shown in reference 1, these are quite as large as the terms retained in his calculation. It appears that because of this difference in treatment, DeBoer obtains agreement with observation for $Z=1.166$, whereas we were forced to assume a greater value.
[3] I. Amdur, J. Chem. Phys. **11**, 157 (1943).

separation are not exact, as is the case in the present instance, a similar effect is to be expected. Neglect of ionic states is one of the more serious approximations made in these calculations.

In the notation of I,

$$H_{AA}=\tfrac{1}{2}(H_{11}+H_{22}-2H_{12}),$$
$$\Delta_{AA}=\tfrac{1}{2}(\Delta_{11}+\Delta_{22}-2\Delta_{12}). \quad (3)$$

When the Hamiltonian function for the three-particle system is written down and use is made of the Schrödinger equations satisfied by a, b, and c, there results

$$H\{a(1)b(2)c(3)\}=\{3D-(1-Z)(\alpha_1+\beta_2+\gamma_3)$$
$$-(\alpha_2+\alpha_3+\beta_1+\beta_2+\gamma_1+\gamma_2)$$
$$+\rho_{12}+\rho_{13}+\rho_{23}+E_N\}a(1)b(2)c(3)$$

where again $D=-\frac{1}{2}Z^2e^2/a_0$, and E_N is the electrostatic energy of the three nuclei. If, in analogy with I, we define

$$\epsilon=(abc|H|abc), \quad u_1=(bac|H|abc),$$
$$u_2=(cba|H|abc), \quad u_4=(acb|H|abc),$$
$$v_1=(bca|H|abc)$$

and denote the corresponding matrix elements of unity by primed symbols, we find

$$H_{11}=\epsilon-u_2, \quad H_{12}=-u_1+v_1, \quad H_{22}=\epsilon-u_4,$$

and hence by (3)

$$H_{AA}=\epsilon+u_1-\tfrac{1}{2}(u_2+u_4)-v_1,$$
$$\Delta_{AA}=\epsilon'+u_1'-\tfrac{1}{2}(u_2'+u_4')-v_1'. \quad (4)$$

The exchange integrals now have the following form:

$$\epsilon=3D+3\kappa A+C_{ab}+C_{ac}+C_{bc},$$
$$u_1=\Delta^2_{ab}\{3D+X_{ab}+B_{ac}+B_{bc}$$
$$+\kappa(A+2T_{ab})+X'_{ab}\},$$

where X'_{ab} now has the simpler form

$$2\frac{(ac\rho bc)-(a\gamma b)}{\Delta_{ab}}, \quad (5)$$

$u_2=u_1$ with interchange of b and c

$u_4=u_1$ with interchange of a and c

$$v_1=\Delta_{ab}\Delta_{ac}\Delta_{bc}\{3D+(\kappa-1)(T_{ab}+T_{ac}+T_{bc})+U_{abc}\},$$

$\kappa\equiv Z-1$.

Henceforth quantities bearing subscripts ab, i.e., pertaining to the *molecule*, will be written without indices. When atom and molecule are very far apart, the exchange integrals above reduce to

$$\epsilon=3D+C+3\kappa A, \quad \epsilon'=1,$$
$$u_1=\Delta^2\{3D+X+\kappa(A+2T), \quad u_1'=\Delta^2,$$
$$u_2=u_4=v_1=0, \quad u_2'=u_4'=v_1'=0.$$

On using these in (4) and (2) there results

$$E^0=3D+\kappa A+\frac{C+2\kappa A+\Delta^2(X+2\kappa T)}{1+\Delta^2}. \quad (6)$$

This, however, is the energy of a single molecule [cf. I, Eq. (15)] plus $D+\kappa A$, an increment which represents the energy of one hydrogen atom computed with the function a, that is, $D+\kappa A=\int a\mathrm{H}_{\mathrm{atom}}a\,d\tau$. Hence, in order to find the exchange energy between the molecule and the atom, it is necessary to subtract E^0 given by (6) from E computed in accordance with Eq. (2).

In proceeding further, prohibitive labor is encountered unless use is made of the reduction described in I. The approximations called for are different when the distance of approach is small and when it is large. We consider the case of very small separations first.

TABLE I. Exchange energies for small distances of separation. Atoms a and b form a molecule. R_{ac} and R_{bc} are the distance of atom c from a and b, respectively. R is the distance of c from center of molecule.

	Z	R_{ac}(A)	R_{bc}(A)	R(A)	$E-E^0$ (ev)
a	1.071	0.57	0.17	0.20	104
b	1.071	0.42	0.42	0.20	72
c	1.071	0.84	0.10	0.47	117
d	1.071	0.60	0.60	0.47	26
e	1.20	0.83	0.09	0.46	142
f	1.20	0.58	0.58	0.45	29
g	1.30	0.82	0.08	0.45	150
h	1.30	0.45	0.45	0.26	56

II. SMALL DISTANCES OF SEPARATION

Let atoms b and c come very close together. It is then necessary to retain all terms in the exchange integrals, but the slowly varying functions bearing indices b and c may be replaced by their limiting forms in which the distance between atoms b and c is put equal to zero. In

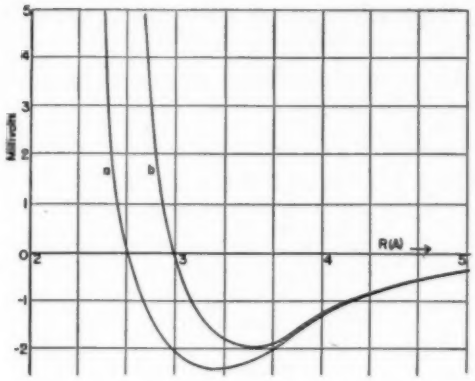

FIG. 1. Interaction between H_2 and H, calculated for $Z=1.071$. Curve a represents approach of H along bisector of molecular axis, curve b along axis.

that case

$$X'_{ab}\rightarrow X'_{ac}\rightarrow M_{ab}-2T_{ab},$$
$$X'_{bc}\rightarrow 2(ab\rho ab)-2(a\beta a),$$
$$U_{abc}\rightarrow X_{ab}+S_{ac}^{-1}+S_{bc}^{-1}-(a\beta a)+M_{ab}.$$

The only function appearing here which was not explicitly given in I is

$$M=2T-\frac{3}{4}\frac{1+2S+(4/9)S^2}{1+S+(1/3)S^2}e^{-S}\left(\frac{Ze^2}{a_0}\right).$$

As before, S is the distance indicated by the subscripts, measured in units a_0/Z.

Computations of E were made for 3 different values of Z and for certain positions of atom c relative to the molecule which were selected for numerical convenience. The results are collected in Table I. It will be noted that cases a, c, e, and g represent positions of atom c on the axis of the molecule, the others on the bisector of the axis. In the former group, the atom is close to one of the molecular nuclei; hence the interaction energy is very large. For these small separations, the distance R between atom and center of the molecule is not a significant parameter. As will appear later, the best value of Z for the present problem is probably near the first of those here chosen. The results indicate, however, that the choice of Z is not very important at these small distances of separation.

Comparison with the results of Amdur[3] yields very poor agreement indeed. If we limit our consideration to cases where the atom is situated on the bisector of the molecular axis—this being the more probable condition of impact—instances d and f should be comparable with the data given by Amdur, who finds approximately 8 and 8.5 ev instead of our 26 and 29 ev. This discrepancy by a factor greater than 3 can hardly be accounted for in its entirety by inaccuracies in the present calculations, or by our omission of ionic terms in the state function. It seems indeed that the assumption of spherical symmetry of the interaction, made in the deduction of the experimental curve from scattering data, must be at fault. The discrepancy is materially reduced if the collision radius in reference 3 is regarded as the distance of closest approach, not to the center of the molecule, but to the nucleus of one of the molecular atoms.

III. LARGE DISTANCES OF SEPARATION

For large distances of separation, a different set of approximations must be made in evaluating E. Numerical computation shows that the quantity X'_{ab} appearing in (5) may be neglected. Furthermore, we split H_{AA} and Δ_{AA} into their

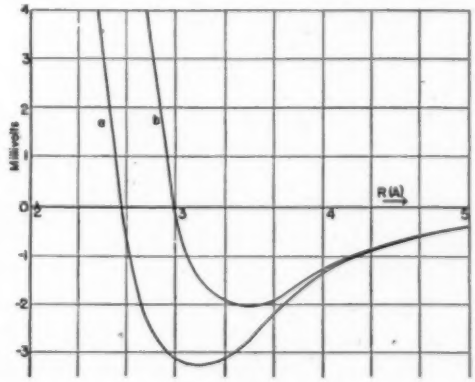

FIG. 2. Interaction between H_2 and H, calculated for $Z=1.20$. Curve a represents approach of H along bisector of molecular axis, curve b along axis.

large and small constituents:

$$H_{AA}=H_{AA}^{(0)}+H_{AA}^{(2)},\quad \Delta_{AA}=\Delta_{AA}^{(0)}+\Delta_{AA}^{(2)},$$

where the large parts $H^{(0)}$ and $\Delta^{(0)}$ are those which were retained in arriving at Eq. (6). Then

$$E=\frac{H_{AA}}{\Delta_{AA}}=\frac{H_{AA}^{(0)}}{\Delta_{AA}^{(0)}}+\frac{H_{AA}^{(2)}}{\Delta_{AA}^{(0)}}-\frac{H_{AA}^{(0)}\ \Delta_{AA}^{(2)}}{(\Delta_{AA}^{(0)})^2},$$

if squares of the small terms are neglected. The

TABLE II. Exchange energy $E=E^0$ in units Ze^2/a_0. S is the distance between the atom and the center of the molecule in units a_0/Z. In position a, the atom lies on the bisector of the molecular axis; in position b, on the axis.

	$Z=1.071$		$Z=1.2$		$Z=1.3$	
S	Pos. a	Pos. b	Pos. a	Pos. b	Pos. a	Pos. b
5	0.(2)1607	0.(2)192	0.(2)332	0.(2)442	0.(2)455	0.(2)644
6	0.(3)331	0.(3)412	0.(3)760	0.(2)1070	0.(2)1119	0.(2)1648
7	0.(4)638	0.(4)748	0.(3)1695	0.(3)238	0.(3)243	0.(3)383
8	0.(4)1015	0.(4)1277	0.(4)323	0.(4)495	0.(4)486	0.(4)822
9	0.(5)1970	0.(5)2141	0.(5)637	0.(5)947	0.(5)983	0.(4)1596
10	0.(6)358	0.(6)379	0.(5)1261	0.(5)183	0.(5)2001	0.(5)334

first of the three fractions on the right of this equation is E^0, hence

$$E-E^0=(\Delta_{AA}^{(0)})^{-1}(H_{AA}^{(2)}-E^0\Delta_{AA}^{(2)}).$$

When all terms on the right are inserted and the exact expression for U_{abc} is replaced by its limiting form for $R_{ab}\to 0$:

$$U_{abc}=\frac{e^2}{s}+X(S)+2T(S),$$

the result is

$$\begin{aligned}E-E^0=(1+\Delta^2)^{-1}\{&C_{ac}+C_{bc}+\Delta^2(B_{ac}+B_{bc})\\&+\tfrac{1}{2}\Delta_{ac}^2[\tfrac{1}{2}E_0'-B-X_{ac}-2\kappa T_{ac}]\\&+\tfrac{1}{2}\Delta_{bc}^2[\tfrac{1}{2}E_0'-B-X_{bc}-2\kappa T_{bc}]\\&+\Delta\Delta_{ac}\Delta_{bc}[\tfrac{1}{2}E_0'-s^{-1}-(\kappa-1)T\\&+\kappa(A-T_{ac}-T_{bc}-X(S))]\}. \quad (7)\end{aligned}$$

The notation is explained in I. If all lengths in this expression are taken in units a_0/Z, the energy is in units Ze^2/a_0.

The choice of Z calls for comment. It would seem at first sight that some mean value between that proper for the molecule and that for the atom should be used. The minimum of the molecular energy occurs for $Z=1.16$; the correct value for the atom is of course 1. In some of our calculations we have taken Z to be 1.071 (which makes $s=1.5$). In our former work (I) on the four-electron problem there appeared a peculiar difficulty: The value of Z corresponding to the minimum of molecular energy produced an attractive exchange force. On analyzing the situation we found reason to accept a larger value of Z, the chief argument involving the greater repulsive effect between the electrons. A similar difficulty does not appear in the three-electron problem; the exchange force is repulsive for all Z that were tried. Nevertheless, if the former argument is valid, a value in the neighborhood of 1.2 should be a better choice. Hence calculations were made for that case. The difference between the results for $Z=1.071$ and 1.2 is surprisingly small. To complete the picture we have also studied $Z=1.3$. But the minimum resulting from the composition of exchange and van der Waals forces is much deeper in that case and may be dismissed from consideration.

Results for $E-E^0$ are given in Table II. In position a, the atom is situated on the bisector of the molecular axis, in b on the axis.

There remains now the calculation of the long range attractive forces. The method is outlined in I. On using for the atom an oscillator strength $f=1$ and a corresponding resonance energy $0.487\ e^2/a_0$ (which gives the correct coefficient of R^{-6} in the interaction between H atoms), we obtain for the dipole-dipole energy

$$E_{2,2}=-8.40\left(\frac{a_0}{R}\right)^6\frac{e^2}{a_0}. \quad (8)$$

The dipole-quadrupole energy, calculated from a formula previously given,[4] becomes

$$E_{2,4}=-148\left(\frac{a_0}{R}\right)^8\frac{e^2}{a_0}. \quad (9)$$

When (7), (8), and (9) are finally compounded, there results the total interaction which is plotted, for 2 values of Z, in Figs. 1 and 2. There are at present no empirical data with which they may be compared. The minimum comes at about the same place as it does for the two similar positions in the bimolecular problem, but it is slightly less deep. The "shape" of the molecule again manifests itself in the differences between curves a and b.

[4] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

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The Forces Between Water Molecules and the Second Virial Coefficient for Water

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In previous work on this subject, the second virial coefficient has been calculated with numerical success, but on the assumption of intermolecular forces which take inadequate cognizance of the known structure of the water molecule. In the present paper, all long range forces are computed in a semi-empirical way from dipole moment, quadrupole moment in accordance with the Bernal-Fowler analysis, and optical dispersion data. Interactions caused by quadrupole moments cannot be neglected. Short range repulsive forces are thus left undetermined. These are chosen in such a way that the second virial coefficient, in its dependence on temperature, approximates its measured values as closely as possible. It is found that a reasonable fit cannot be obtained with the use of the hard sphere model, nor with any model which permits the polar component of the force to be effective at arbitrarily small distances of separation. More satisfactory agreement results if the polar forces are eliminated at all distances smaller than the potential minimum. The best potential satisfying these various requirements is given at the end of the paper [formula (22)].

INTRODUCTION

THE present paper has as its principal purpose the determination of the forces acting between water molecules. To this end, we rely on the theory of van der Waals forces to provide an expression for the interaction at large distances of separation. The short range repulsive forces are at present beyond purely theoretical treatment. It might be expected, however, that when the attractive forces are known, available empirical data, such as the values of the second virial coefficient at different temperatures, would fix within reasonable limits the repulsive forces as well. This will prove to be the case.

To give a general survey, we list first the various types of forces which compose the total interaction and state their physical origins. Among the long range forces there are: (1) The attractions or repulsions between the permanent multipoles borne by a water molecule. These include not only the customary dipole forces to which the attention of most writers has been limited, but also quadrupole and higher types. For it will be seen that H_2O carries a sizable quadrupole moment whose presence may not be neglected. Since the Boltzmann factor makes alignment of the multipoles more probable than other orientations, the net effect, called alignment effect, is attractive. (2) Attractions caused by the induction of additional multipole moments by the fields of permanent moments—the so-called induction effect. (3) The forces arising from a mechanism similar to the preceding, but through fields caused by the rapidly rotating moments associated with electronic motions within a molecule instead of permanent moments. This is known as the dispersion effect. It is present regardless of whether the molecule has a multipole or not.

The short range forces are repulsive; their origin lies partly in the electrostatic repulsion between the molecular nuclei, partly in electron exchanges. They are not of spherical symmetry, but their angular dependence has not been described for the case of water molecules.

We now give a brief survey of the history of the present problem. The theory describing effect (1) of the preceding paragraph was developed by Keesom[1] at the time when all van der Waals forces were thought to originate in permanent multipoles. His treatment of dipole interactions is adequate for the problem at hand; his work on quadrupoles, which considers only *linear* structures, is in need of generalization before application to water molecules can be made. Furthermore, Keesom considers molecules having *only* a dipole, or *only* a quadrupole moment. The exact treatment for the combination of both is very unwieldy and will not be attempted here; an approximation will suffice for our purposes.

[1] W. H. Keesom, Physik. Zeits. 22, 129 (1921).

The induction effect was considered by Debye[2] and Falkenhagen.[3] Formulas developed by them may be used in this work. For the theory of dispersion forces introduced by London, we refer the reader to a review article by one of the authors.[4]

An early analysis of the H_2O problem[5] which included consideration of all effects here mentioned resulted in the prediction that the molecule, in order to produce virial coefficients of the known magnitudes, possesses a quadrupole moment of about 5×10^{-26} e.s.u. In this work, the repulsive forces were treated somewhat inadequately, their effect being described by an infinite repulsion at a distance of separation equal to the kinetic theory diameter. (Hard sphere model.) This fiction, frequently employed in the past, makes the results extremely sensitive to the choice of that diameter, which is empirically ill defined and therefore sometimes leads to a specious semblance of success. Wohl[6] and Briegleb,[7] using similar methods and approximations, discussed the situation from a general chemical point of view.

More recently, the problem has been reconsidered by Stockmayer.[8] He shows that the temperature behavior of the second virial coefficients of water and ammonia is described with numerical correctness by assuming the molecules to be *point* dipoles. His calculation permits much latitude in the choice of other parameters of the interaction and shows, in fact, that the forces producing such agreement are far from unique. In a sense, this type of success is satisfying, but it teaches very little about the actual properties of the molecule and augments our knowledge in no fundamental way. Since our prime concern is with the actual forces, the assumption of point dipoles is inadequate.

The work of Goff, Anderson, and Gratch[9] contains the significant indication that the hard sphere model, when used in conjunction with a plausible set of force parameters, is not capable of yielding the correct temperature dependence of the second virial coefficient for water. This is true even when the essentially spherical force field, employed as an approximation by these authors, is replaced by a field of dipole symmetry as will later be shown in this paper.

We consider the various effects of interest in the order in which they were listed in the second paragraph of this introduction.

INTERACTION BETWEEN PERMANENT MULTIPOLES

For the sake of completeness and systematic development, we include in this section a few results that are known. The method is perhaps more direct than those found in the earlier literature.

Let a set of discrete point charges e_i be situated at vector distances $\mathbf{r}_i=(x_i, y_i, z_i)$ from an origin 0. Another set of charges ϵ_λ is placed at distances $\boldsymbol{\varrho}_\lambda=(\xi_\lambda, \eta_\lambda, \rho_\lambda)$ from an origin Ω; the displacement of Ω relative to 0 is $\mathbf{R}$. The mutual static potential energy between these sets is then

$$V=\sum_{i\lambda}\frac{e_i\epsilon_\lambda}{|\mathbf{R}-\mathbf{r}_i+\boldsymbol{\varrho}_\lambda|}.$$

If we introduce "relative displacement vectors" $\boldsymbol{\sigma}_{i\lambda}=\mathbf{r}_i-\boldsymbol{\varrho}_\lambda$, V can be expressed in two equivalent simple forms, the operator form

$$V=\sum_{i\lambda}e_i\epsilon_\lambda\exp\left(-\boldsymbol{\sigma}_{i\lambda}\cdot\nabla\right)\left(\frac{1}{R}\right), \qquad (1)$$

which results from a Taylor development, and the Legendre form

$$V=\sum_{i\lambda}\frac{e_i\epsilon_\lambda}{R}\sum_l P_l(\cos\alpha_{i\lambda})\left(\frac{\sigma_{i\lambda}}{R}\right)^l, \qquad (2)$$

obtainable on application of a well-known expansion theorem in terms of Legendre polynomials. In the last expression, $\alpha_{i\lambda}$ is the angle between $\boldsymbol{\sigma}_{i\lambda}$ and $\mathbf{R}$: $\cos\alpha_{i\lambda}=(z_i-\zeta_\lambda/\sigma_{i\lambda})$ provided we take the Z axis along $\mathbf{R}$, as will henceforth be understood. Equation (2) is the more useful for our present purposes. If

$$\sum_i e_i=\sum_\lambda\epsilon_\lambda=0,$$

[2] P. Debye, Physik. Zeits. **21**, 178 (1920).
[3] H. Falkenhagen, Physik. Zeits. Sowjetunion **23**, 87 (1922). For a correction to this paper, see reference 5.
[4] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).
[5] H. Margenau, Phys. Rev. **36**, 1782 (1930).
[6] K. Wohl, Zeits. f. physik. Chemie **B23**, 105 (1933).
[7] G. Briegleb, Zeits. f. physik. Chemie **B14**, 36 (1931).
[8] W. H. Stockmayer, J. Chem. Phys. **9**, 398 (1941).
[9] J. A. Goff, J. R. Anderson, and S. Gratch, Heating, Piping and Air Conditioning **15**, 319 (1943).

as we are supposing, the terms for which $l=0$ and 1 make no contribution to (2). For sufficiently compact charge distributions and sufficiently large R, this series converges rapidly. In most molecular problems, terms beyond $l=4$ need not be considered. To this approximation, insertion of the Legendre polynomials gives

$$\begin{aligned}V=&-(1/R^3)\sum_{\substack{i\\ \lambda}} e_i\epsilon_\lambda(2z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda)\\&+(3/2R^4)\sum_{\substack{i\\ \lambda}}e_i\epsilon_\lambda[r_i^2\zeta_\lambda-z_i\rho_\lambda^2\\&+(2x_i\xi_\lambda+2y_i\eta_\lambda-3z_i\zeta_\lambda)(z_i-\zeta_\lambda)]\\&+(3/4R^5)\sum_{\substack{i\\ \lambda}}e_i\epsilon_\lambda[r_i^2\rho_\lambda^2-5z_i^2\rho_\lambda^2-5r_i^2\zeta_\lambda^2\\&\quad-15z_i^2\zeta_\lambda^2+2(4z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda)^2]\\&+(1/2R^5)\sum_{\substack{i\\ \lambda}}e_i\epsilon_\lambda[3(r_i^2+\rho_\lambda^2)\\&\times(4z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda)\\&\quad+5(z_i^2+\zeta_\lambda^2)(3x_i\xi_\lambda+3y_i\eta_\lambda-4z_i\zeta_\lambda)]. \quad (3)\end{aligned}$$

Summations 1 to 4 represent, respectively, dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, dipole-octupole interactions.

In physical problems, it is usually necessary to calculate

$$\int \exp(-V/kT)\sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\varphi,$$

$$\equiv \int \exp(-V/kT)d\Omega, \quad (4)$$

θ_1 and θ_2 being the polar angles between fixed lines in the molecules and Z, φ the relative azimuth. If only the first summation of V is retained, this integral can be evaluated exactly, for V then has the simple form

$$-(p_1p_2/R^3)(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi), \quad (5)$$

where the p's are dipole moments. But in general, a series expansion of $\exp(-V/kT)$ must be performed before integration. The number of terms to be retained in this series depends on T. In the application to be made later, one should strictly use terms up to V^{10}, but the labor involved in such a computation appears prohibitive. We therefore adopt the following approximate procedure.

Since $\int V^n d\Omega$ vanishes for odd n, the first term which occurs in the expansion is $\int V^2 d\Omega$. This will be computed exactly for the whole of expression (3). For sufficiently high temperatures this is the decisive contribution to (4), though that is not true in our application. We then evaluate (4) including the dipole term only, but augmenting the coefficient p_1p_2/R^3 in (5) in the proper way so that the mean square of the approximate V is nearly equal to $\int V^2 d\Omega$. This will require the addition of a term in R^{-5} to p_1p_2/R^3, a term characteristic of the quadrupole interaction. We proceed now to the calculation of $\int V^2 d\Omega \equiv 8\pi\langle V^2\rangle_{Av}$.

In squaring V, the cross terms between different summations of Eq. (3) may at once be omitted, for they will be seen to vanish when the integration over angles is performed. A great number of others may also be omitted; the justification for this curtailment will appear later on. The significant terms to be retained are given here in part:

$$\begin{aligned}V^2=&(1/R^6)\sum e_ie_je_\lambda e_\mu(4z_iz_j\zeta_\lambda\zeta_\mu\\&+x_ix_j\xi_\lambda\xi_\mu+y_iy_j\eta_\lambda\eta_\mu)\\&+(9/4R^8)\sum e_ie_je_\lambda e_\mu(r_i^2r_j^2\zeta_\lambda\zeta_\mu\\&+z_iz_j\rho_\lambda^2\rho_\mu^2+4x_ix_jz_iz_j\xi_\lambda\xi_\mu+\cdots)\\&+(9/16R^{10})\sum\cdots+(1/4R^{10})\sum\cdots. \quad (6)\end{aligned}$$

To obtain $\langle V^2\rangle_{Av}$ it is thus necessary to compute averages of the type $\langle x_i^n x_j^m\rangle_{Av}$, $\langle x_i^n y_j^m\rangle_{Av}$, etc. This procedure is somewhat complicated by the fact that the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ are not independent—since the whole molecule is being oriented in the evaluation of the averages in question—but lie along rays always making a fixed angle θ_{ij} at 0. However, averages over Greek and Latin letters may be carried out independently because they refer to different molecules.

A convenient method for carrying out the averaging process with respect to connected coordinates appears to be this. We introduce Euler angles α, β, γ and let $\boldsymbol{R}(\alpha,\beta,\gamma)$ be the matrix which, when applied to the vector $\mathbf{r}$, produces rotation about the origin through α,β,γ. Starting with any special, permitted position of the vectors $\mathbf{r}_1$[10] and $\mathbf{r}_2$ such as

$$\mathbf{r}_1^0=r_1\mathbf{k}, \quad \mathbf{r}_2^0=r_2(\sin\theta_{12}\mathbf{j}+\cos\theta_{12}\mathbf{k}),$$

[10] We now write 1, 2 for the former indices i, j.

we obtain their most general position by applying to them the matrix R:

$$\mathbf{r}_1 = R\mathbf{r}_1^0, \quad \mathbf{r}_2 = R\mathbf{r}_2^0.$$

These vectors have components

$$\begin{array}{l|l} x_1 = -r_1 \sin\beta\cos\gamma & x_2 = r_2\sin\theta_{12}(\sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma) - r_2\cos\theta_{12}\sin\beta\cos\gamma \\ y_1 = r_1\sin\beta\sin\gamma & y_2 = r_2\sin\theta_{12}(-\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma)+r_2\cos\theta_{12}\sin\beta\sin\gamma \\ z_1 = r_1\cos\beta & z_2 = r_2\sin\theta_{12}\sin\alpha\sin\beta+r_2\cos\theta_{12}\cos\beta. \end{array}$$

The desired average over any quantity Q is then simply

$$\langle Q\rangle_{Av} = \frac{1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma Q,$$

with θ_{12} held fixed and Q expressed through the preceding relations. The results needed here are:

$$\begin{array}{ll} \langle x_i x_j\rangle_{Av} = (1/3) r_i r_j \cos\theta_{ij} & \langle x_i y_i x_j y_j\rangle_{Av} = (1/30) r_i^2 r_j^2 (3\cos^2\theta_{ij} - 1) \\ \langle x_i y_j\rangle_{Av} = 0 & \langle x_i y_i z_j^2\rangle_{Av} = 0 \\ \hline \langle x_i^3 x_j\rangle_{Av} = (1/5) r_i^3 r_j \cos\theta_{ij} & \langle x_i y_i z_i z_j\rangle_{Av} = 0 \\ \langle x_i^2 x_j^2\rangle_{Av} = (1/15) r_i^2 r_j^2 (1+2\cos^2\theta_{ij}) & \langle x_i y_j z_j^2\rangle_{Av} = 0 \\ \langle x_i^3 y_j\rangle_{Av} = 0 & \langle x_i y_j x_j z_j\rangle_{Av} = 0 \\ \hline \langle x_i z_i z_j^2\rangle_{Av} = 0 & \langle z_i^2 z_j^2 x_i x_j\rangle_{Av} = r_i^3 r_j^3 \dfrac{4\cos^3\theta_{ij} - \cos\theta_{ij}}{105} \\ \langle x_i^2 y_j^2\rangle_{Av} = (1/15) r_i^2 r_j^2 (1+\sin^2\theta_{ij}) & \langle z_j^3 z_j^3\rangle_{Av} = r_i^3 r_j^3 \dfrac{2\cos^3\theta_{ij} + 3\cos\theta_{ij}}{35} \\ \langle x_i x_j y_j^2\rangle_{Av} = (1/15) r_i r_j^3 \cos\theta_{ij} & \langle z_i^2 x_i z_j^2 y_j\rangle_{Av} = 0 \\ & \langle z_i^2 x_i z_j^3\rangle_{Av} = 0. \end{array} \tag{7}$$

In addition to this list we note that averages over terms of odd power, such as x^2y, are always zero. Many other relations may be produced by noting two operations with respect to which the formulas above are invariant: (1) interchange of any two coordinates; (2) interchange of the indices i and j throughout. If averages over higher powers of V than the second were needed, similar integrations over a greater number of connected coordinates would have to be performed.

Combination of (6) and (7) yields finally a relatively simple result for $\langle V^2\rangle_{Av}$:

$$\begin{aligned} \langle V^2\rangle_{Av} = \sum_{\substack{ij\\ \lambda\mu}} e_i e_j e_\lambda e_\mu \Big\{ & \frac{2}{3R^6} r_i r_j P_1(\cos\theta_{ij}) \rho_\lambda \rho_\mu P_1(\cos\theta_{\lambda\mu}) \\ & + \frac{1}{R^8}\big[r_i^2 r_j^2 P_2(\cos\theta_{ij}) \rho_\lambda \rho_\mu P_1(\cos\theta_{\lambda\mu}) \\ & + r_i r_j P_1(\cos\theta_{ij}) \rho_\lambda^2 \rho_\mu^2 P_2(\cos\theta_{\lambda\mu})\big] \\ & + \frac{14}{5R^{10}} r_i^2 r_j^2 P_2(\cos\theta_{ij}) \rho_\lambda^2 \rho_\mu^2 P_2(\cos\theta_{\lambda\mu}) \\ & + \frac{4}{3R^{10}}\big[r_i^3 r_j^3 P_3(\cos\theta_{ij}) \rho_\lambda \rho_\mu P_1(\cos\theta_{\lambda\mu}) \\ & + r_i r_j P_1(\cos\theta_{ij}) \rho_\lambda^3 \rho_\mu^3 P_3(\cos\theta_{\lambda\mu})\big] \Big\}. \end{aligned} \tag{8}$$

The P's are again Legendre polynomials. Here, obviously, the θ's with Latin indices refer to one, those with Greek indices to the other molecule. This answer, the general form of which (though hardly the numerical coefficients appearing in it) could have been predicted from symmetry considerations, immediately suggests the introduction of certain invariants:

Dipole-invariant: $L = \sum_{ij} e_i r_i e_j r_j P_1(\cos\theta_{ij})$,

Quadrupole-invariant: $M = \sum_{ij} e_i r_i^2 e_j r_j^2 P_2(\cos\theta_{ij})$,

Octupole-invariant: $M = \sum_{ij} e_i r_i^3 e_j r_j^3 P_3(\cos\theta_{ij})$.

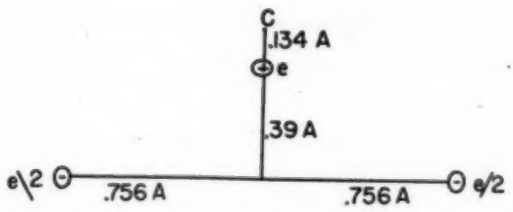

FIG. 1. Electrical structure of the water molecule assumed in calculation of moments. *Note:* In the figure the minus signs should be plus, and the plus sign should be minus.

Equation (8) then takes the form

$$\langle V^2\rangle_{Av}=\frac{2}{3R^6}L^{(1)}L^{(2)}+\frac{1}{R^8}(M^{(1)}L^{(2)}+L^{(1)}M^{(2)})$$
$$+\frac{1}{R^{10}}\left[\frac{14}{5}M^{(1)}M^{(2)}+\frac{4}{3}(L^{(1)}N^{(2)}+N^{(1)}L^{(2)})\right]. \quad (9)$$

The invariants may also be expressed as functions of multipole moments. On defining, as usual,

$$\text{dipole moment}=\mathbf{p}=\sum_i e_i\mathbf{r}_i,$$

components of quadrupole moment

$$=Q_{zz}=\sum_i e_i x_i^2, \qquad Q_{xy}=\sum_i e_i x_i y_i, \text{ etc.},$$

components of octupole moments

$$=O_{zzz}=\sum_i e_i x_i^3, \quad O_{xzy}=\sum_i e_i x_i^2 y_i, \text{etc.},$$

they read:

$$\begin{aligned}
L&=p^2,\\
M&=Q_{zz}^2+Q_{yy}^2+Q_{zz}^2+(3Q_{xy}^2-Q_{zz}Q_{yy})\\
&\quad+(3Q_{xz}^2-Q_{zz}Q_{zz})+(3Q_{yz}^2-Q_{yy}Q_{zz}),\\
N&=O_{zzz}^2+O_{yyy}^2+O_{zzz}^2+6O_{xxy}^2+6O_{zzz}^2+6O_{xyy}^2\\
&\quad+6O_{yyz}^2+6O_{zzz}^2+6O_{yzz}^2+15O_{xyz}^2\\
&\quad-3O_{zzz}(O_{zyy}+O_{zzz})-3O_{yyy}(O_{zzy}+O_{yzz})\\
&\quad-3O_{zzz}(O_{zzz}-O_{yyz})-3O_{zzz}O_{yyz}\\
&\quad-3O_{zzy}O_{zzy}-3O_{zyy}O_{zzz}.
\end{aligned} \quad (10)$$

We now return to our original plan for the calculation of $\int \exp(-V/kT)d\Omega$. This involved the replacement of the correct V of Eq. (3) by an approximate V' of the form

$$V'=-\left[\frac{L}{R^3}+u(R)\right]f$$

where

$$f=2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\varphi$$

in such a way that $\langle V^2\rangle_{Av}=\langle V'^2\rangle_{Av}$ as nearly as possible. Since $\langle f^2\rangle_{Av}=\frac{2}{3}$ we have

$$\langle V'^2\rangle_{Av}=\frac{2}{3}\left[\frac{L^2}{R^6}+\frac{2Lu}{R^3}+u^2\right].$$

On comparing this with (9), in which all superscripts may now be omitted because we are dealing with two similar molecules, we find $u=(3M/2R^5)$ so far as the first two terms on the right of (9) are concerned. This choice makes the contribution of the $1/R^{10}$ term somewhat too small for the case of H_2O, but this is not a serious matter since that contribution turns out to be small anyway. Henceforth, then, we use

$$V=-\left(\frac{L}{R^3}+\frac{3}{2}\frac{M}{R^5}\right)f(\theta_1\theta_2\varphi). \quad (11)$$

In calculating the constants of Eq. (10) for the water molecule we have assumed the electrical structure proposed by Bernal and Fowler,[11] who place a charge $+\frac{1}{2}e$ at each of the H nuclei, and a charge $-e$ on the bisector of the H−H distance, 0.20A away from the 0 nucleus. The mass structure, needed to locate the center of mass about which quadrupole and octupole moments must be computed, is that determined by Mecke and Baumann.[12] Details are depicted in Fig. 1, where C represents the center of mass. They give the known value $p=1.87\times10^{-18}$ e.s.u. for the dipole moment. Furthermore, we find

$$L=35.2\times10^{-37}\text{ e.s.u.}, \quad M=56.6\times10^{-53}\text{ e.s.u.},$$
$$N=99.6\times10^{-69}\text{ e.s.u.}$$

With these values, Eq. (9) becomes

$$\langle V^2\rangle_{Av}=\left(\frac{8.27\times10^{-72}}{R^6}+\frac{39.9\times10^{-88}}{R^8}+\frac{183\times10^{-104}}{R^{10}}\right)\text{ergs}^2. \quad (12)$$

At $R=3$A, which is near the distance of closest approach of two molecules, the three terms here retained are, respectively, 11.3, 6.1, and 3.1

[11] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[12] R. Mecke and W. Baumann, Physik. Zeits. Sowjetunion **33**, 833 (1932). K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

$\times 10^{-27}$ erg^2 which shows that omission of the quadrupole moment entails a very serious error. On the other hand, the approximate V of Eq. (11) becomes

$$V=-\left(\frac{3.52\times10^{-36}}{R^3}+\frac{8.50\times10^{-52}}{R^5}\right)f(\theta_1\theta_2\varphi). \quad (13)$$

It gives a $\langle V^2\rangle_{Av}$ which agrees with (12) in the first two terms, of course, but makes the coefficient of the last term much too small (48.2 instead of 183). This, however, will be regarded as acceptable in view of the inaccuracies of the model.

INDUCTION EFFECT

In describing the induction effect, the analysis of reference 4 will be followed. If the potential energy produced by one molecule at the position of the other is φ, the energy induced in the latter is $-\frac{1}{2}\alpha(\nabla\varphi)^2$, where α is the molecular polarizability. To be sure, this energy depends on the orientation of the inducing molecule (and to the extent to which α is a tensor upon the orientation of the other as well), but this dependence is much less pronounced than in the preceding effect. In particular, the energy cannot change sign. Instead of introducing an angular function in the integral $\int \exp(-V/kT)d\Omega$, we shall therefore average over directions at once. This leads to the induction energy

$$-\tfrac{1}{2}\alpha\langle(\nabla\varphi)^2\rangle_{Av}=-\alpha\left(\frac{L}{R^6}+\frac{3}{2}\frac{M}{R^8}+\cdots\right), \quad (14)$$

wherein L and M are the former invariants. For the two interacting molecules, this expression has to be multiplied by 2. In the next section, reasons will be given for choosing the value of α to be 1.44×10^{-24} cm^3. We thus obtain as the contribution of the induction effect to the intermolecular energy in water

$$V=-\left(\frac{10^{-59}}{R^6}+\frac{24\times10^{-76}}{R^8}+\cdots\right)\text{ergs}. \quad (15)$$

The leading term of this expression is only about 10 percent of the first part of (13) at $R=3$A, which indicates the relative importance of the two effects.

DISPERSION EFFECT

The dispersion effect produces an interaction energy also of the form $-(C/R^6)-(D/R^8)$. The value of C calculated in reference 4 and used in previous work on the second virial coefficient[8,9] was obtained with the use of London's[13] formula in which the "resonance" energy was set equal to the ionization energy of the molecule, and α was taken to be 1.5×10^{-24} cm^3. This procedure can be improved by employing optical dispersion formulas, two of which are available.[14]

Dorsey,[15] in his valuable compendium on water, assumes as the best value of the polarizability $\alpha=1.59\times10^{-24}$ cm^3. This is derived from Stranathan's[16] and other measurements of the dielectric constants. As might be expected in that type of work, the measurements are somewhat discordant, and Stranathan admits a possible error of 10 percent in α.

On the other hand, Dorsey lists, without comment on the implied discrepancy, two one-term dispersion formulas, one due to Cuthbertson,

$$n-1=\frac{2.63\times10^{27}}{10700\times10^{27}-\nu^2}, \quad (16)$$

and one proposed by Hölemann and Goldschmidt,

$$n-1=\frac{3.07\times10^{27}}{12500\times10^{27}-\nu^2}. \quad (17)$$

They permit computation of α by extrapolation to $\nu=0$. Both yield $\alpha=1.44\times10^{-24}$ cm^3. We believe this extrapolation to be more accurate than the former value and shall, therefore, use it in the present work.

In a similar way, the force parameters C and D will be computed from (16) and (17). Equation (16) involves a resonance energy of 13.55 ev and an oscillator strength of 2.41; the respective quantities in (17) being 14.7 and 2.81 ev. Both resonance energies are smaller than the ionization energy (18 ev). The constant D may be computed from a formula previously published.[17]

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[13] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).
[14] C. and M. Cuthbertson, Phil. Trans. **A213**, 1 (1913). P. Hölemann and H. Goldschmidt, Zeits. f. physik. Chemie **B24**, 199 (1934).
[15] N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940).
[16] J. D. Stranathan, Phys. Rev. **48**, 538 (1935).
[17] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

This procedure leads to $C=33.7\times10^{-60}$ erg cm^6, $D=95\times10^{-76}$ erg cm^8 on the basis of (16); $C=36.4\times10^{-60}$ erg cm^6, $D=95\times10^{-76}$ erg cm^8 from (17). The value of D is to be regarded as quite uncertain. We take as the contribution of the dispersion effect to the intermolecular potential

$$V=-\left(\frac{35\times10^{-60}}{R^6}+\frac{95\times10^{-76}}{R^8}\right)\text{ ergs.} \quad (18)$$

SECOND VIRIAL COEFFICIENT

After determination of all constituents of the long range van der Waals energy, attention will now be directed to the short range repulsive forces. Concerning them there is but meager information. Attempts to derive specific details from a large variety of empirical data led us to abandon the search for a potential the uniqueness of which could plausibly be accepted before calculating the equation of state:

$$\frac{pv}{RT}=1+\frac{B}{v}+\cdots,$$

in particular the second virial coefficient B. The procedure has therefore been inverted: The repulsive potential is to be determined by seeking agreement with known values of B at different temperatures.

Two facts, however, may be assumed. A survey of the material on the crystal structure of ice,[18] considerations by Bernal and Fowler, the density of water, etc., indicate that the minimum of the total potential must lie somewhere between 2.7 and 2.9A. While the concept of a minimum has no precise meaning for forces which depend on angles, this realization nevertheless proves to be a guide. It is possible, for example, to calculate the average orientation of adjacent water molecules in ice and fix the minimum with some precision. The value of R chosen for this was about 2.80A. Such deliberations, however, serve only for preliminary orientation; it develops that choices widely different from this do not yield proper values of B.

The second fact concerns the form of the repulsive force law. Calculations on simpler molecules and atoms of spherical symmetry show that the exchange energy, in a sufficiently large range of distances, may be represented in the form $A\exp(-R/\rho)$, which will here be chosen.

At first thought, then, one would try a total potential pieced together from (13), (15), (18) and the latter expression, i.e.,

$$V=a(R)+b(R)f(\theta_1,\theta_2,\varphi) \quad (19)$$

in which[19]

$$a(R)=A\exp(-R/\rho)-\left(\frac{45\times10^{-60}}{R^6}+\frac{119\times10^{-76}}{R^8}\right),$$

$$b(R)=\frac{3.52\times10^{-36}}{R^3}+\frac{8.5\times10^{-52}}{R^5}.$$

The parameters A and ρ are not quite as disposable as they might seem, even if no condition is imposed on the position of the minimum. The condition that there be a minimum at all drastically limits the choice. Result (19) is to be inserted into the well-known formula

$$B=2\pi N^2\int^\infty R^2dR\int_\Omega(1-\exp(-V/kT))\frac{d\Omega}{8\pi}. \quad (20)$$

The second integration yields

$$1-\exp[-a(R)/kT]\int\exp(-bf/kT)\frac{d\Omega}{2\pi}=1-\exp(-a/kT)F(b/kT).$$

Let $b/kT\equiv x$. Then

$$F(x)=\sum_\lambda\int\frac{(-xf)^\lambda}{\lambda!}\frac{d\Omega}{8\pi}=\sum_{n=0}^\infty\int\frac{(xf)^{2n}}{(2n)!}\frac{d\Omega}{8\pi},$$

the last because $\int f^\lambda d\Omega=0$ for odd λ. Now

$$\int f^{2n}\frac{d\Omega}{8\pi}=\frac{1}{2n+1}\cdot\frac{2.4\cdots2n}{1\cdot3\cdots(2n+1)}\sum_{l=0}^n\binom{2l}{l}\equiv G_{2n},$$

[18] W. H. Bragg, Proc. Phys. Soc. London **34**, 98 (1922). B. E. Warren, J. Chem. Phys. **6**, 666 (1938).

[19] Because of an oversight, a different value of the coefficient in the last term of $a(R)$ has been used in the subsequent numerical calculations. We have, unfortunately, neglected the quadrupole moment in computing the induction effect, so that the coefficient in question was 95 instead of 119. Revision was not made because this term makes only a minor contribution to B and is not known with sufficient accuracy.

TABLE I. Comparison of experimental and calculated values of B in cm³/mole on the basis of the hard sphere model.

T	B_{calc}	B_{exp}	Rel. error
700°K	−65.9	−65.4	−0.8 percent
600°K	−112.4	−99.0	−13.5 percent
500°K	−215.2	−166.4	−29.3 percent
400°K	−542	−346.9	−56.2 percent

TABLE II. Comparison of experimental and values of B in cm³/mole calculated on the assumption of a potential minimum.

T	B_{calc}	B_{exp}	Rel. error
700°K	−65.9	−65.4	−0.8 percent
600°K	−109.9	−99.0	−11 percent
500°K	−200.2	−166.4	−20 percent

so that

$$F(x)=\sum_{n=0}^{\infty}\frac{G_{2n}}{(2n)!}x^{2n}. \tag{21}$$

While it is quite possible to integrate e^{-zf} without expansion—the result being either a series in Bessel functions or a definite integral over Bessel functions—the present form of $F(x)$ has been found most convenient for problems of this type. We have prepared a numerical table of $F(x)$ with x ranging from 0 to 10. The remaining integration,

$$B=2\pi N\int R_2\left\{1-\exp\left[-a(R)/kT\right]F\left[\frac{b(R)}{kT}\right]\right\}dR$$

was carried out graphically. This is much less tedious than expansion of the integrand and subsequent term-by-term integration.

If $A\to\infty$ while $\rho\to 0$, V reduces to the potential characteristic of hard spheres. This was one of the first models tried. It involves only one disposable parameter, and this is adjusted by making B come out correctly at one temperature. Measurements with which comparison is here made are those of Keyes, Smith, and Gerry.[20]

In the calculation with the hard sphere model, only the attractive terms of the potential are used. If the infinite barrier is placed at $R=2.87$A, sufficient agreement results for $T=700$°K. Table I shows what happens at lower temperatures.

This outcome, while at first unpleasant, is particularly interesting in view of the fact that Stockmayer[8] was able to obtain good agreement at all temperatures with the use of the hard sphere model, when he neglected the quadrupole moment. The discrepancies incurred can, however, be made to tell us more about the repulsive interaction. They are due, it seems, to the large coefficient of the angular part of the potential, which makes a proportionately larger contribution to B at lower temperatures. We therefore attempt to neutralize this effect by using finite values for A and ρ.

A typical calculation involved the use of $\rho=0.28$A (a value in this neighborhood seems to be required in order to produce a minimum at all; cf. also the findings of R. Heller[21]) and $A=3.155\times10^{-9}$ erg. These correspond to a potential minimum, computed with the proper value of f as explained, at 2.80A. The results are given in Table II. While the correct B is obtained at 700°K, the same sort of discrepancy appears at lower temperatures, though it has diminished somewhat in magnitude. Numerous trials were made with other sets of parameters, notably those corresponding to a minimum at 2.76A (0−0 distance in ice), at 2.90A (intermolecular distance in liquid water), and at 3.10A. These yielded no better success.

The conclusion is therefore inescapable that a potential of the form (19) cannot be used for the purpose at hand. This might indeed have been expected, for it implies that the function f, which is characteristic of polar behavior, is effective all the way into the origin $R=0$. On the other hand, the repulsive potential which is taken to be independent of angles provides no mechanism for counteracting this fictitious polarity at close distances of separation. A more reasonable representation of the potential appears to be this. Assume the polar forces to be active for $R>R_{min}$, the range in which the molecules may indeed be regarded as permanent multipoles. But for $R<R_{min}$, let all interactions be of spherical symmetry. Though the latter hypothesis is but an approximation to the truth, it is a better approximation than the very extreme and specific one of dipolar symmetry.

Such a representation does not yield a con-

[20] F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. Arts Sci. 70, 319 (1936).

[21] R. Heller, J. Chem. Phys. 9, 154 (1941).

tinuous curve for all orientations of the molecules. This analytic fault will have to be accepted in order to avoid the artificial difficulties which the construction of a continuous function would entail. Thus we take

$$V=\begin{cases} V_1=a'(R), & R<R_{\min} \\ V_2=a(R)+b(R)f(\theta_1\theta_2\varphi) & R>R_{\min}, \end{cases}$$

where a' differs from a in having a different set of constants A', ρ'. For A and ρ, the preceding calculations strongly suggest 3.25×10^{-9} erg, $\rho=0.28$A as most likely values. This leaves A' and ρ' to be determined. There appears to be some latitude in their choice, and we cannot be sure that the adjustment here proposed is unique. But the effect of reasonable alterations on B is not large.

One relation between them will be obtained by requiring continuity between V_1 and V_2 at $R_{\min}$, that is, at 2.80A for some definite temperature, say 700°K. Thus

$$\exp(-V_1/kT)=\int\exp(-V_2/kT)\frac{d\Omega}{8\pi}$$
$$=\exp[-a(R)/kT]\cdot F[b(R)/kT]$$

at $T=700$°K and $R=2.80$A. (If this fit were tried at $R=2.90$A, it would require the use of a negative A'. This again shows one of the self-stabilizing aspects of the procedure.) The second relation is provided by the requirement that B shall have its experimental value at some temperature at the middle of the range. The work involved here is obviously tedious, and no claim will be made that the present investigation is exhaustive; slightly different values of the constant may produce an even better fit. On taking $A'=2.4\times10^{-6}$ erg, $\rho'=0.15$A—a model which approaches the hard sphere case—the temperature dependence of B (see Table III) is obtained. While the agreement is not perfect, the improvement is very considerable and indicates that the repulsive potential adopted is not far from correct.

TABLE III. Experimental and calculated values of B in cm³/mole by use of adjusted constants.

T	B_{calc}	B_{exp}	Rel. error
700°K	−68.9	−65.4	−5.4 percent
600°K	−101.1	−99.0	−2.1 percent
500°K	−164.4	−166.4	+1.2 percent
400°K	−329.8	−346.9	+4.9 percent

The small quantum correction, computed by Stockmayer[8] for dipoles, does not improve the calculated values materially. An estimate for the present case shows that it reduces the error at 700°K to about −5 percent while increasing that at 400°K to about 5.5 percent.

Summarizing the work, we find that

$$V=\begin{cases} 2.4\times10^{-6}\exp(-R/0.15\text{A})-c(R) & \text{if } R<2.80\text{A} \\ 3.25\times10^{-9}\exp(-R/0.28\text{A}) & \\ \quad -c(R)-b(R)(2\cos\theta_1\cos\theta_2 & \\ \quad -\sin\theta_1\sin\theta_2\cos\varphi) & \text{if } R>2.80\text{A} \end{cases} \tag{22}$$

with

$$c(R)=\left(\frac{45\times10^{-60}}{R^6}+\frac{95\times10^{-76}}{R^8}\right)\text{ergs},$$

$$b(R)=\left(\frac{3.52\times10^{-36}}{R^3}+\frac{8.50\times10^{-52}}{R^5}\right)\text{ergs}$$

represents the best intermolecular potential for water molecules in view of available facts.

The Production of Photons Relative to Ionization by Collision in a Townsend Gap

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(Received September 29, 1944)

Measurements were made in a Townsend gap to determine the average number of photons liberated by an electron for each secondary electron it liberates. In H_2, this number was found to decrease rapidly with increasing ratio of field strength to gas pressure in the range from 50 to 150 volts/cm/mm, and at pressures of the order of 1 mm. Determination of the absolute number of photons per electron depends on the unknown efficiency of the photoelectric cell used to count the photons. However, this number is estimated as of order unity. The effective radiation has an absorption coefficient of 0.55 cm^{-1} at a pressure of 1 mm of Hg. This large coefficient indicates that only those photons of rather high energy were counted. There is corroborative evidence that the brass surface of the photoelectric cell had a high work function. Thus only high energy photons would be expected to register.

INTRODUCTION

PHOTO-IONIZATION is increasingly accepted as an active mechanism responsible, at least in part, for the appearance of the second Townsend coefficient. In 1934, Cravath,[1] investigating the corona discharge, found that photoelectric effects were produced both in the gas and at the cathode. Dechene,[2] in the following year, showed the same phenomena to be present in corona and sparks. Kenty,[3] working with the positive column, and Greiner,[4] with Geiger counters, also contributed important evidence of photoelectric action. Photoelectrons produced in the gas by a spark were found by Raether[5] who detected them with a cloud chamber. The studies of Bowls[6] and Hale[7] have indicated that in certain cases the second Townsend coefficient can be attributed almost entirely to photoelectric effects at the cathode. Recent work on corona discharge[8-11] by investigators at the University of California has shown the dependence of this phenomenon on photoelectric effects in the gas. Raether's[12] investigations, and Loeb and Meek[13] in their book, have demonstrated that the streamer

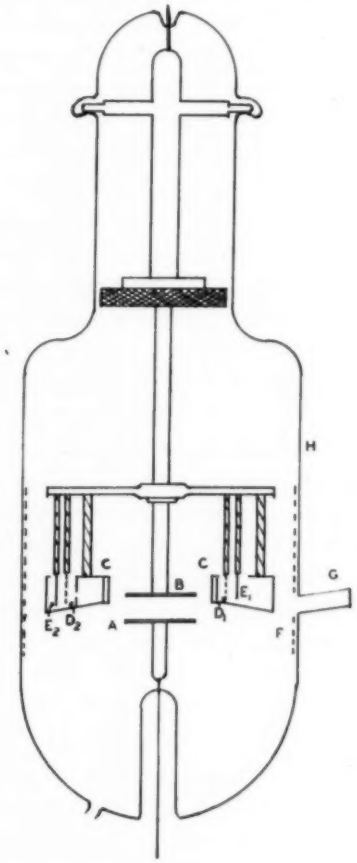

FIG. 1. Arrangement of chamber. *A*, cathode; *B*, anode; *C*, "doughnut;" D_1, D_2, collecting screens; E_1, E_2, measuring electrodes; *F*, grounded screen; *G*, quartz graded seal and window; *H*, Pyrex envelope.

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[1] A. M. Cravath, Phys. Rev. **47**, 254 (1935).
[2] G. Dechene, J. de phys. et rad. **7**, 533 (1936).
[3] Carl Kenty, Phys. Rev. **44**, 891 (1933).
[4] E. Greiner, Zeits. f. Physik **81**, 543 (1933).
[5] H. Raether, Zeits. f. Physik **110**, 611 (1938).
[6] W. E. Bowls, Phys. Rev. **53**, 293 (1938).
[7] D. H. Hale, Phys. Rev. **54**, 241 (1938); *ibid.* **55**, 815 (1939).
[8] A. F. Kip, Phys. Rev. **54**, 139 (1938); *ibid.* **55**, 549 (1939).
[9] G. W. Trichel, Phys. Rev. **54**, 1078 (1938); *ibid.* **55**, 382 (1939).
[10] S. Gorril, Thesis, (University of California, 1939).
[11] Loeb, Hudson, Kip, and Bennett, Phys. Rev. **60**, 714 (1941).
[12] H. Raether, Zeits. f. Physik **107**, 91 (1937); *ibid.* **112**, 464 (1939).
[13] L. B. Loeb and J. M. Meek, *The Mechanism of the Electric Spark* (Stanford University Press, 1941).

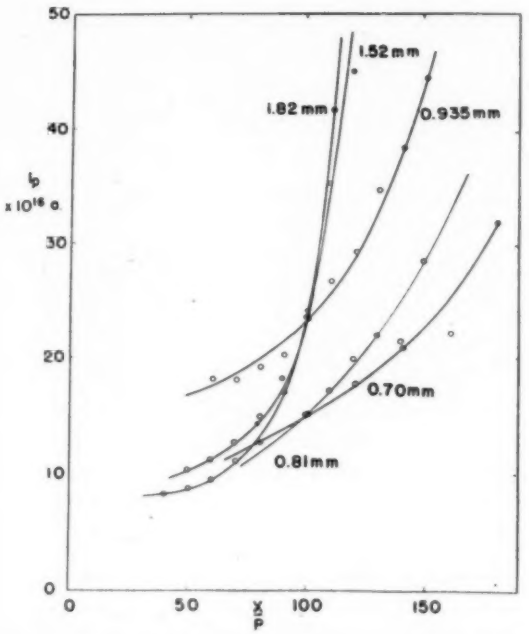

FIG. 2. Photoelectric currents at pressures of 0.70 mm, 0.81 mm, 0.935 mm, 1.52 mm, and 1.82 mm of Hg as functions of X/p.

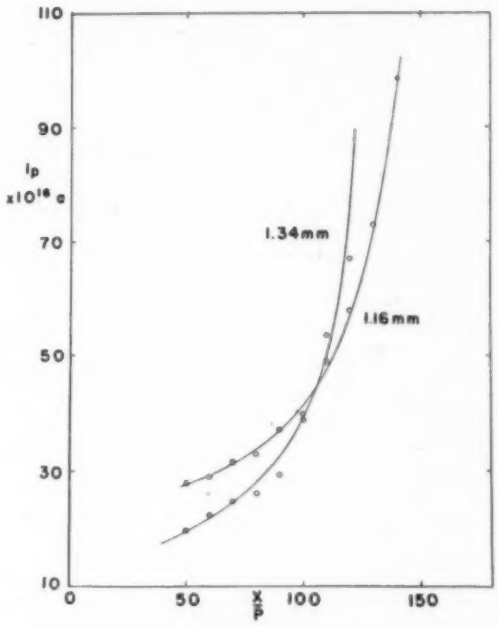

FIG. 3. Photoelectric currents at pressures of 1.16 mm and 1.34 mm of Hg as functions of X/p.

theory of spark discharge requires the assumption of an adequate supply of photoelectrons. Penning[14] has made calculations of the efficiency of electrons in ionizing and exciting gas molecules, these efficiencies being given as functions of field strength divided by pressure (X/p in volts/cm/mm). However, he was forced to use data of a doubtful nature and to extrapolate the data to extreme values.

In view of the incomplete nature of the above data, it was felt desirable that experiments be performed which would give an indication of the quantity of photons produced in a Townsend discharge. This paper sets forth the results of such an investigation, the gas used being H_2. Measurements made by Dr. L. H. Fisher in a number of other gases will be reported in the near future.

Consider a function θ defined as the number of photons produced by an electron in traveling one cm in the field direction of a discharge. In analogy with Townsend's α it is to be expected that

$$\theta/p = F(X/p). \tag{1}$$

From θ and α we may construct a function

$$n(X/p) = \theta/\alpha. \tag{2}$$

This represents the number of photons produced by an electron for each secondary electron it produces. The function $n(X/p)$ lends itself readily to the calculations to follow. θ, α, and n are defined for a uniform field, in which case X/p determines the mean energy of the electrons.

Let i_0 be the initial electron current liberated from the cathode of a plane-parallel gap, which cathode is illuminated with ultraviolet light from a mercury arc. Then in the interval dx, at a distance x from the cathode, $i_0\alpha e^{\alpha x}dx$ secondary electrons will start. Hence, in this interval, $ni_0\alpha e^{\alpha x}dx$ photons will be produced in the gas. The measuring apparatus will count only those photons which pass through a slit system and liberate electrons from a brass electrode. Thus the solid angle subtended by the slit at each point of the discharge must be calculated. It is assumed that the photons are directed isotropically. At the low pressures (of the order of 1 mm of Hg) necessary in this experiment, diffusion of the electrons becomes appreciable and must be included in the calculation. It is also necessary to correct for the absorption of the photons by gas molecules. This correction, to a sufficient accuracy, is made by a factor $\exp[-\mu_0 P p]$ where μ_0 is the average absorption coefficient at 1 mm of

[14] F. M. Penning, Physica 5, 286 (1938).

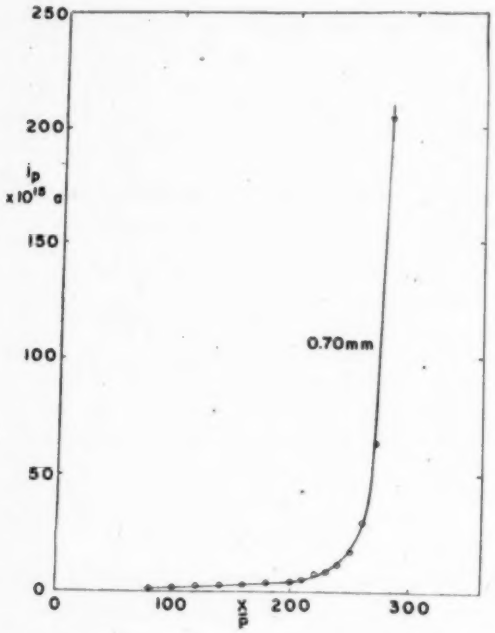

FIG. 4. Photoelectric current at 0.70 mm of Hg for X/p up to 280.

Hg and ρ is the distance from the center of the discharge to the collecting electrode.

Performance of the necessary integration leads to the expression

$$n\left(\frac{x}{p}\right)=\frac{34.0}{\eta}\frac{i}{i_e}\exp\left[\mu_0 p\rho\right]h(\alpha)$$
$$=n_p\exp\left[\mu_0 p\rho\right]. \quad (3)$$

Here η is the photo-efficiency of the brass counting surface, to be discussed later; i is the measured photoelectric current; $i_e=i_0e^{\alpha\delta}$ is the total electron current to the anode; $h(\alpha)$ is a function calculated from the geometry; and n_p is the quantity actually found by measurement, as the absorption coefficient is not known beforehand. μ_0 can be determined from values of n_p at two different pressures as well as from two electrodes at different distances from the discharge.

DESCRIPTION OF APPARATUS AND PROCEDURE

The chamber, originally designed by J. M. Meek, is shown diagrammatically in Fig. 1. A is the cathode, upon which ultraviolet light falls through the quartz window G. The anode B and measuring electrode system C, E, and D can be raised and lowered together by means of a screw-thread, ball-bearing race, and an iron armature turned by an external electromagnet. D is a screen kept at +22.5 volts to remove electrons liberated from the brass electrode. The "doughnut," containing the slit system, was kept at a constant potential of −67.5 volts. E, D, and C are insulated from each other by quartz supports. F is a nickel screen kept at ground potential. H is the glass envelope. The electrodes A and B are 4.0 cm in diameter, and are parallel to better than 0.5°. The inside diameter of the "doughnut" is 6.0 cm. Plate separations were read by means of a cathetometer.

The sets of collecting electrodes E_1, D_1 and E_2, D_2 are at 4.5 and 6.0 cm from the center, respectively, and were used as a pair to make measurements of the absorption coefficient. E_1 and E_2 could be connected to a Dolezalek electrometer through sulphur-insulated platinum switches. The sensitivity of the electrometer was 1500 mm/volt, and the capacity of the system including E_1, the cable, and the electrometer was 96.5 cm.

The anode B was kept at ground potential, and a negative voltage applied to A. This potential was supplied either by batteries or by a voltage stabilizer. An Heraeus mercury arc was used as a source of ultraviolet light. The image of a slit, illuminated by the arc, was focused on the cathode. The arc was operated on storage batteries and gave a quite constant intensity. The

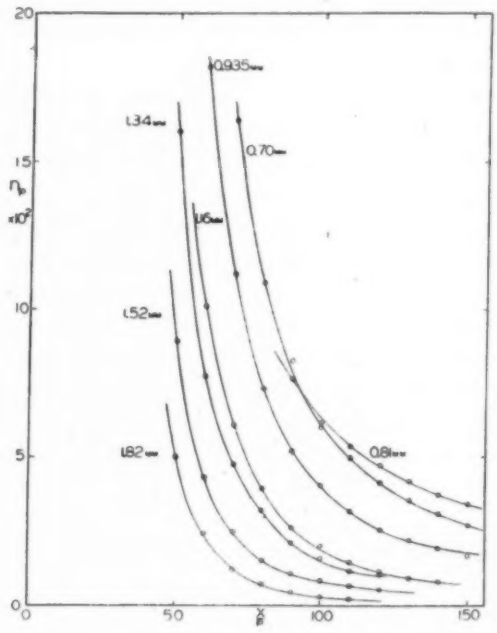

FIG. 5. n_p as a function of X/p for various pressures.

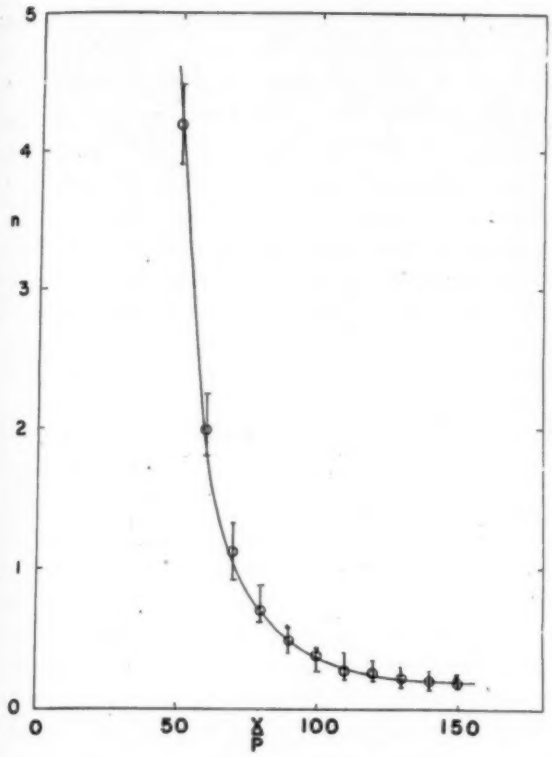

FIG. 6. The number of photons per secondary electron, n, as a function of X/p. Ordinates must be divided by the photoelectric efficiency to obtain absolute values. Vertical lines indicate spread.

visible image was rectangular, about 0.5 cm by 2 cm.

The photoelectric current was measured by the rate of charging of the electrometer. Backgrounds were determined with voltages applied but ultraviolet light cut off. They were occasionally as low as 10^{-16} ampere, and in most cases less than 0.1 of the photoelectric current. To keep the field distortion as constant and small as possible, all measurements were made at the smallest plate distance, 1.39 cm.

The total electron current to the anode was determined for each photoelectric measurement. This was necessary since the "doughnut" produced considerable field distortion. The plate separation could not be made less than 1.39 cm without interfering with the beam of ultraviolet light. Thus, measurements on the linear portion of the $\ln i_e/i_0$ *vs.* plate distance curve were impossible for X/p in excess of 110. Values of α under these conditions were determined by measuring i_0 at lower X/p and using this quantity and the total electron current i_e at the X/p desired. It is interesting to note that in spite of the large and variable field distortion, the graphs of $\ln i_e/i_0$ *vs.* plate distance are unmistakably linear at low X/p. The current i_e was determined by reading the voltage drop across a 10^8-ohm S. S. White resistor, or if too large for this, a 10^7-ohm I. R. C. calibrated resistor.

The chamber was baked out at 200°C and 10^{-5} to 10^{-6} mm of Hg for several hours. Measurements were made in two fillings of the chamber. Tank H_2 was passed over Cu at 350°C and then through a spiral liquid air trap. The chamber, of 6 liters volume, was filled to pressures of 1 to 2 mm of Hg in a period of approximately one-half hour. A McLeod gauge was used to read pressures. At no time was the chamber opened to the rest of the vacuum system without the presence of liquid air around the trap.

EXPERIMENTAL RESULTS

Measurements were made from X/p 40 to X/p 150. In one case the current was followed up

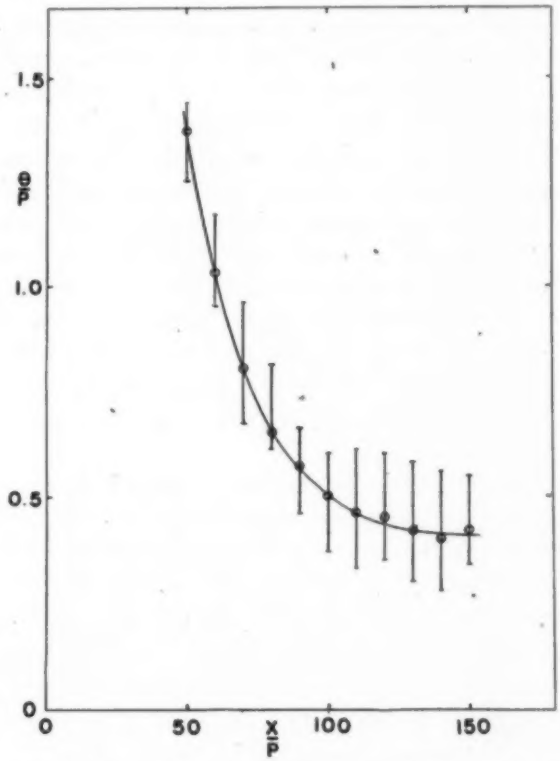

FIG. 7. The number of photons produced per cm per mm of Hg, θ/p, as a function of X/p. Ordinates must be divided by the photoelectric efficiency to obtain absolute values. Vertical lines indicate spread.

to an X/p of 280. The observed variation of photoelectric current at various pressures is shown in Figs. 2 to 5.

Values of n_p were calculated from the observed data and the function $h(\alpha)$. These values are given in Fig. 6 in arbitrary units. To obtain absolute quantities they must be divided by η, the photoelectric efficiency of the brass counting surface, which is unknown.

Independent determinations of the absorption coefficient, one at constant plate separation and the other at constant pressure, give 0.55 cm^{-1} and 0.42 cm^{-1}, respectively, at one mm of Hg. Correction of n_p for absorption brings the curves together, as shown in Fig. 7. The spread in values is indicated by the vertical lines. This spread is comparable with that in the measured α.

DISCUSSION AND CONCLUSION

Penning[14] has made calculations of the percentages of electron energy picked up in the field which appear as excitation, ionization, and in other forms. He has plotted these percentages as functions of X/p. The result of dividing the excitation curve by that for ionization is a variation similar to that in Fig. 7. His curve would remain at high values for low X/p. The design of the present chamber precludes knowledge of conditions at low α, hence, low X/p, and so this aspect cannot be verified. A quantitative comparison with Penning's calculations would require a knowledge of two additional quantities: (1) the photo-efficiency of the counting electrode; (2) the fraction of the total excitation energy represented by those photons capable of releasing electrons from the electrode. These quantities are not known for the experimental arrangement under consideration.

Since the counting surface was not degassed, but was in equilibrium with H_2 at a pressure of one or two mm, a value of η approaching 0.5 is not unlikely. If we assume this as a rough estimate, then at an X/p of 80 and at 1 mm of Hg, we find θ is about one photon/cm. From extrapolated data of Townsend and Bailey,[15] Bradbury and Nielsen,[16] and the kinetic free path, it is found that the number of collisions made by an electron per cm of path in the direction of the field under the above conditions is of the order of 100. Thus the inelastic collisions resulting in photons of the energies here considered represent a percent or so of the total number.

Hale's[7] curves for γ in H_2, with Pt and NaH cathodes, show a photoelectric peak in the neighborhood of $X/p=140$. The absence of such a phenomenon in the present work may be explained by one or both of the following: (1) Such a peak may not appear with a brass electrode; (2) the brass electrode may have such a high work function that the photons responsible for the peaks found by Hale are not sufficiently energetic to register. Calculations of γ for the anode show it to be of the order of 0.001, a tenth or less of Hale's values. Thus the brass surfaces present in the chamber are not photoelectrically sensitive.

Raether[5] has reported an absorption coefficient in H_2 of 0.9 cm^{-1} at 760 mm of Hg. His measurements were made above 235 mm of Hg. Greiner[4] gives a coefficient equivalent to 1.4 cm^{-1} at 760 mm of Hg measured at pressures of the order of 100 mm of Hg. At such high pressures any component of radiation with an absorption coefficient as large as that found in the present work would not be measured. It thus appears that the brass electrodes have surfaces of a particularly insensitive nature and are affected by only the most energetic photons.

Weissler[17] has shown that in a positive point-to-plane corona in pure H_2 no pre-onset streamers occur. Since the present work indicates that in such a discharge photons are produced in an appreciable quantity, it can only be concluded that either they are not sufficiently energetic for photo-ionization in the gas, or are absorbed too slowly to contribute photoelectrons to the formation of a streamer.

In conclusion, the author wishes to express gratitude to Professor L. B. Loeb, without whose guidance this undertaking would have been impossible. He also thanks Dr. Leon H. Fisher for many helpful discussions, and Mr. E. H. Guyon, glassblower, for his patience and skill.

[14] F. M. Penning, Physica **5**, 286 (1938).
[15] Townsend and Bailey, Phil. Mag. **42**, 873 (1921).
[16] N. E. Bradbury and R. A. Nielsen, Phys. Rev. **49**, 388 (1936).
[17] G. L. Weissler, Phys. Rev. **63**, 96 (1943).

The Mesotron Momentum Spectrum at 4.35-km Altitude

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The mesotron momentum spectrum has been determined at Mount Evans, Colorado, from the shape of the absorption curve in lead as measured by Geiger-Müller counter telescopes. Special attention was paid to eliminating the contribution of single electrons to the measured intensity. A large number of low energy mesotrons were found, resulting in a sharp maximum of the momentum spectrum lying between 1 and 2×10^8 ev/c. A simple power law is not adequate to describe the spectrum in the entire region investigated.

INTRODUCTION

THE mesotron spectrum at intermediate altitudes has usually been approximated in calculations by assuming a distribution in energy similar to that found at sea level.[1–4] The function generally used has been in the form of a power law with an exponent of about 3, extending from about 10^9 ev to very high energies. In the present investigation, the distribution was determined by absorption measurements in lead, with thicknesses extending from 0.5 cm to 91.5 cm of lead. Because the mesotrons lose energy in solid material by ionization processes only, and therefore have a definite range depending only on the thickness of material traversed and the energy of the particle, a lower energy limit can be assigned to those mesotrons which are able to penetrate any given thickness of material. The expressions for energy loss as a function of material traversed, such as the Bethe-Bloch formula, have been well tested and found to be reliable at least in the region of 2 to 7×10^8 ev.[5] The formulae given by B. Rossi and K. Greisen[6] were found convenient to use here. Since the absorption curve of mesotrons represents an integral spectrum of these particles, the usual form of differential energy spectrum can be directly obtained from the experimental points. For convenience in comparison with cloud-chamber measurements, the results to be given are expressed as momenta, in units of ev/c, bearing the usual relation to energy of $E=(p^2+\mu^2)^{\frac{1}{2}}-\mu^2$, where the mass of the mesotron has been taken as 10^8 ev/c^2, corresponding to 200 electron masses.[7]

EXPERIMENTAL PROCEDURE

The experiments were carried out at the Mount Evans Laboratory, Colorado (4.35-km altitude, 45.7-cm Hg pressure). Two independent Geiger-Müller counter-tube telescopes shown in Fig. 1 were used. The individual counting rates were adjusted for best agreement at two points. In the arrangement of Fig. 1a, counter tubes were connected in pairs and arranged to give fourfold coincidence between counter pairs 1, 2, 3, and 4, measured with a recording set having a resolving power of about 10^{-4} second. Each set

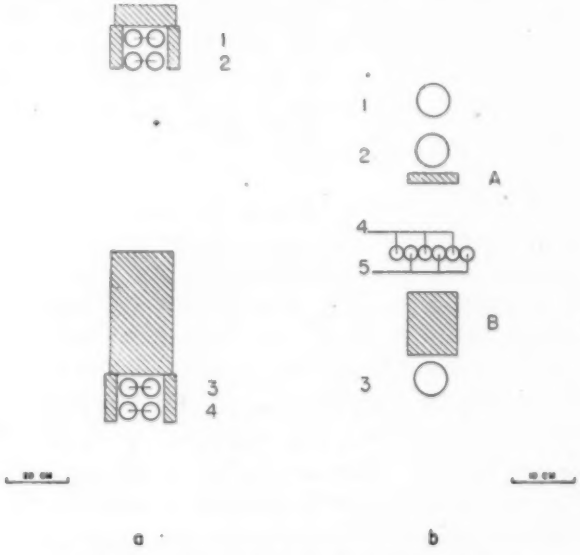

FIG. 1. Arrangement of counters and absorbers.

[1] P. M. S. Blackett and R. B. Brode, Proc. Roy. Soc. **A154**, 573 (1936).
[2] P. M. S. Blackett, Proc. Roy. Soc. **A159**, 1 (1937).
[3] Hayden Jones, Rev. Mod. Phys. **11**, 235 (1939).
[4] D. J. Hughes, Phys. Rev. **57**, 592 (1940).
[5] J. G. Wilson, Proc. Roy. Soc. **A172**, 517 (1939).
[6] B. Rossi and K. Greisen, Rev. Mod. Phys. **13**, 240 (1941).
[7] L. Le Prince Ringet, E. Nageotte, S. Gorodetzky, and R. Richard Fory, Zeits. f. Physik. **120**, 588 (1943).

of four tubes was housed in 5 cm of lead to reduce the effects of soft side showers. In order to correct for penetrating side showers, the two boxes were placed at the same height so that one particle could not cause a coincidence. This correction, which was of the order of 4 percent, was subtracted from the measured intensity for each thickness of absorber used. No scattering correction was made since, with the counter arrangement used, the chance for scattering into coincidence is almost the same as for scattering out of coincidence. Absorber thicknesses ranging from 15 cm to 91.5 cm of lead were used in this arrangement. The lower limit of 15 cm of lead was sufficient to assure that only mesotrons were being detected.

The arrangement shown in Fig. 1b was used with absorber thicknesses from 0 to 20 cm of lead. Coincidences of counters 1, 2, 3 which defined the solid angle subtended by the vertical telescope were recorded with a circuit of higher resolving power ($\tau = 10^{-5}$ sec.). Corrections for side showers were determined by measuring out of line coincidences with the top counter displaced. With less than 10 cm of lead in the telescope it became necessary to distinguish between mesotrons and electrons. This was done by placing a 1.5-cm lead block in position A and recording the resultant showers of two or more particles emerging from the lead, coincident with a discharge of counters 1, 2, 3. These fivefold discharges of the combined shower and vertical set could be caused by (a) knock-on electrons from the lead block A accompanying mesotrons, (b) electrons generating a cascade shower in lead A, (c) air showers.

Only those events of type (b) were subtracted from the measured vertical intensity (coincidence 1, 2, 3). Events (c) have no relation to the absorber B and only provide a constant background counting rate for the shower set (4, 5). These events (c) were determined by measuring the counting rate with the lead A removed. Type (a) was separated from (b) in order that the correction contains effects owing only to incident electrons. This separation was accomplished by assuming that 10 cm of lead in position B would be sufficient to stop all electrons which entered the apparatus as single particles. Those electrons of high enough energy to penetrate 11.5 cm would have high probability of being accompanied by additional particles when entering the apparatus, and hence would be eliminated by the displaced counter measurements. After the background was eliminated, the frequency of fivefold coincidences with 10 cm of lead in position B was taken to be owing to knock-on electrons accompanying mesotrons. To a first-order approximation at least, this type of event is a constant percentage of the incident mesotrons. The increase, then, in the rate of shower-producing rays with decreasing thickness of absorber in position B was attributed to the electron component of the total cosmic-ray intensity. Corrections were made for the change in efficiency of the shower tray for different energies of incident electrons.

CALCULATIONS

The efficiency of the shower-detecting tray as a function of the number of particles emerging from the lead A can be calculated from the geometrical arrangement of the counter tubes. The number of particles to be expected from electrons of various energies was estimated from Rossi and Greisen's discussion of the cascade process.[6] In calculating the efficiency of the shower tray, it was assumed that in order for the bottom counter 3 to be discharged, at least one particle must have gone through the area covered by the tray and discharged one of the counters belonging to either 4 or 5. The problem then becomes the determination of the compound probability that (a) if N particles emerge from the lead block A, what is the chance that they will emerge in such a direction as to fall within the area of the tray, and (b) what is the chance that the tray will respond to these particles since only half of the area is available for registering a coincidence. Let P_n be defined as the probability that if N particles emerge from the lead *exactly* n of them will strike the tray; let p_n be the probability that if n particles fall in the sensitive area, the tray will register a coincidence. The probability of detecting an N-fold shower may then be written as

$$\Pi_N = \sum_{n=1}^{N-1} P_n p_n.$$

The value of P_n was estimated from the data on

cascade showers reported by Froman and Stearns.[8] For the experimental arrangement of Fig. 1b, at least 80 percent of the shower particles should emerge from the lead in such a direction that they will fall within the active area of the tray. This value was assumed to be independent of the total amount of absorber in the telescope. The error introduced by this assumption will tend to discriminate against the showers produced by high energy electrons where the efficiency of detection is already high and the frequency is expected to be low. The value of p_n was taken as 0.5 since the six tubes comprising the tray were connected so that alternate ones were in parallel. Any inefficiency of the counter tubes themselves which was of the order of 1 percent could be neglected as a second-order effect.

The initial energy of an electron required to penetrate a given thickness of absorber and emerge with one descendant was estimated from calculations of the cascade theory as developed by Arley[9] and also by Rossi and Greisen.[10] From the same calculations, the number of particles to be expected after passing through 1.5 cm of lead was determined for each incident energy. The change in shower-producing rays observed with changing thickness of absorber could then be ascribed to certain energy ranges of incident electrons and an estimate made of the probable size of showers accompanying these rays. This permitted assigning an average efficiency of detection to each range of absorbing thickness. Table I lists the result of these calculations; their application to the data is given in Table II.

EXPERIMENTAL RESULTS

The experimental results are listed in Table III and shown graphically in Fig. 2. The values of $N(e)$ cannot be interpreted accurately as an energy spectrum of the electron component, since (a) air showers, and consequently high energy electrons, have been eliminated, and (b) the penetration of cosmic-ray electrons is not an exact measure of their energy. The value given for the electron intensity at 0.5 cm is an extrapolated figure. The mesotron intensity at 0 cm was taken so that the number of very slow mesotrons, which are heavily ionizing, was limited to less than one percent of the total intensity, in agreement with cloud-chamber studies at this altitude.[11] The resulting spectrum, however, is not sensitive to either of these extrapolations.

TABLE I. Results of calculation of efficiency of detection of electrons.

Total absorber cm of Pb	Min. energy of incident electron	No. of assoc. particles of $E>10$ Mev below 1.5 cm of Pb	Efficiency assigned
1.5	0.5×10^8 ev	1	0.40
3.5	2.0×10^8 ev	4	0.90
5.5	5.5×10^8 ev	10	1.00
11.5	$20.\times10^8$ ev	100	

TABLE II. The electron intensity corrected for efficiency of detection. The measured intensity was adjusted by subtracting the contribution owing to air showers (0.24 c.p.m.) and knock-on electrons. This latter component was estimated to be one percent of the vertical penetrating particles from measurements with 11.5 cm of lead.

Total absorber cm of Pb	Vertical intensity c.p.m.	5-fold shower and vertical combination c.p.m.	Electron intensity c.p.m.	Electron intensity (corrected) c.p.m.
1.5	7.00	0.98	0.67	1.06
3.5	6.10	0.73	0.43	0.46
5.5	5.43	0.43	0.14	0.14
7.5	5.02	0.32	0.03	0.03
11.5	4.57	0.28	0.00	0.00

TABLE III. Compilation of data. $N_{(t)}$ is the measured vertical intensity together with the standard deviation of the measurements; $N_{(e)}$ is the electron correction taken from Table II. $N_{(m)}$ is the resultant vertical mesotron component; $I_{(m)}$ gives the mesotron intensity in percentages of the total.

Cm of Pb	Minimum momentum $\times10^8$ ev/c	$N(t)$ c.p.m.	Std. dev.	$N(e)$	$N(m)$ corrected	$I(m)$ %
0	0	9.50	.09		6.25	100
0.5	0.65	8.20	.09	2.00	6.20	99.4
1.5	0.95	7.00	.08	1.06*	5.94	95.0
3.5	1.35	6.10	.11	.46	5.64	90.2
5.5	1.70	5.43	.07	.14	5.29	84.6
7.5	2.00	5.02	.08	.03	4.99	79.9
11.5	2.50	4.57	.08	.00	4.57	73.0
15.2	3.00	4.33	.04		4.33	69.2
20.3	3.70	4.15	.07		4.15	66.5
30.5	5.00	3.49	.07		3.49	55.8
50.8	7.80	2.83	.07		2.83	45.3
91.5	13.75	2.08	.05		2.08	33.3

* Note that the electron component at 1.5-cm lead corresponds to about 18 percent of the total mesotron intensity. Considering a minimum energy of 1×10^8 ev for these electrons, this is consistent with results recently reported by W. E. Hazen, Phys. Rev. 65, 67 (1944).

[8] D. Froman and J. C. Stearns, Rev. Mod. Phys. 10, 157 (1938).
[9] N. Arley, Proc. Roy. Soc. 168, 519 (1938).
[10] B. Rossi and K. Greisen, reference 6, p. 309.
[11] C. A. Nielsen and W. M. Powell, Phys. Rev. 63, 384 (1943).

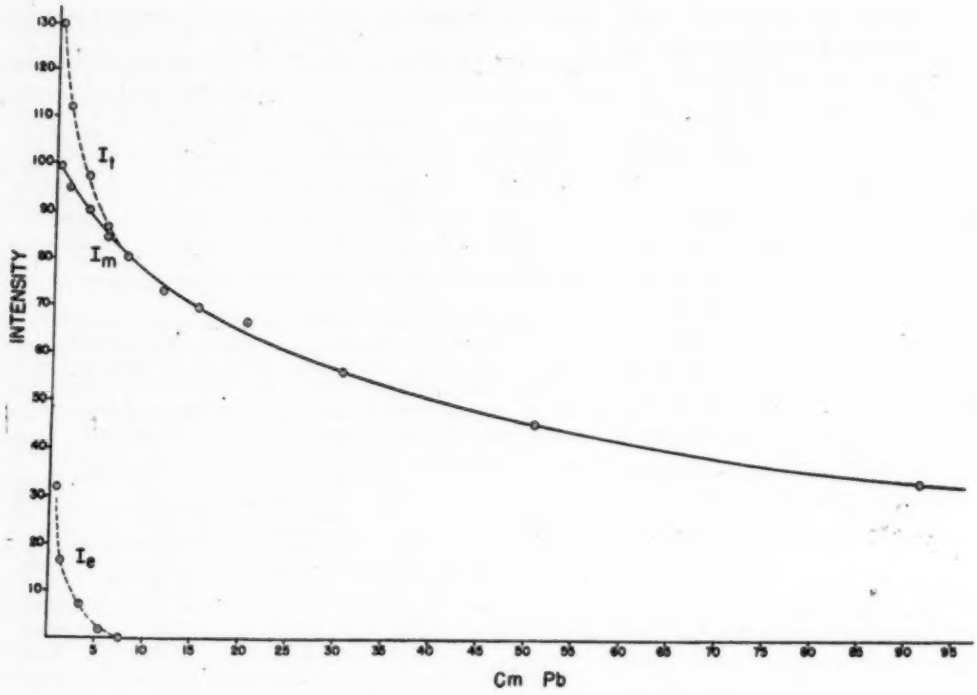

FIG. 2. Absorption of cosmic radiation at Mount Evans, Colorado (el. 4.35 km). It represents the total measured intensity I_t, the shower-producing component after correcting for efficiency. The difference curve I_m gives the mesotron absorption adjusted to be 100 at 0 cm.

Figure 3 is obtained from the smooth curve of Fig. 2. The units are percent of total intensity per hundred million electron volts. The shape of the entire spectrum cannot be represented by a simple mathematical function. Between 2×10^8 ev/c and 10^9 ev/c, however, a rough fit can be obtained for the momentum spectrum of mesotrons by $dN/dP = Ap^{-1.4}$, where A represents an arbitrary constant. In view of the very different spectrum observed at sea level, there is no justification in extending this analytical expression to predict the shape of the curve beyond the region covered by the experimental data.

The presence of the prominent maximum in

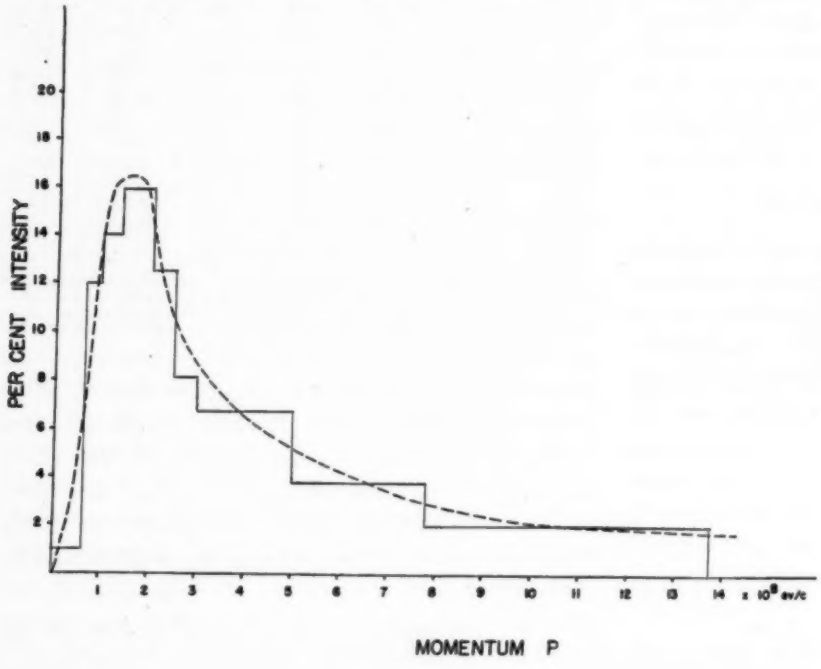

FIG. 3. Differential momentum spectrum at Mount Evans (4.35 km). Abscissa is momenta values obtained by range-momenta relationships. Ordinate is the percent of total intensity per interval of 10^8 ev/c.

the region between 1 and 2×10^8 ev/c cannot easily be accounted for on the usual basis of a mesotron production layer at 16 km and subsequent spontaneous decay in the atmosphere. The shift of the maximum to lower energies and the large number of mesotrons between 10^8 and 10^9 ev/c would require special assumptions in regard to the distribution with which they are created. It is highly probable, therefore, that many of these mesotrons are created relatively close to the point of observation (Mount Evans). Since the number of protons observed near this altitude[11] does not seem large enough to be the principal agent of production, neutral radiation, such as photons or other neutral particles, may be responsible for most of these low energy mesotrons. Although these production processes at low altitudes have been discussed before,[12,13] the importance of their contribution in the description of the spectrum has not been emphasized.

If the observed momentum distribution of Fig. 3 is used to calculate a mesotron spectrum for the elevation of Echo Lake, Colorado (3.24 km), using the usual formulae for decay and ionization loss, one obtains a curve shown in Fig. 4 that is in reasonably good agreement with the data obtained by anticoincidence measurements of Rossi, Greisen, Stearns, Froman, and Koontz[14] taken at this station. This would indicate that the mesotron production processes do not contribute an appreciable quantity of mesotrons in the energy range between 3×10^8 to 12×10^8 ev for altitudes intermediate between that of Mount Evans and Echo Lake.

Since only mesotrons of momenta greater than

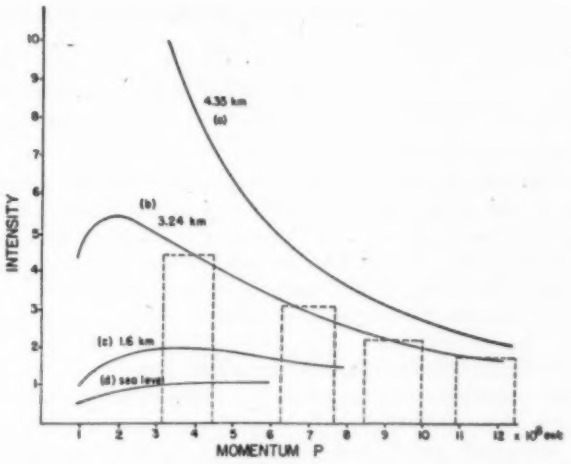

FIG. 4. Mesotron momentum spectra at several altitudes. Curve (*a*) is the measured curve for Mount Evans (4.35 km), curves (*b*), (*c*), and (*d*) are calculated from curve (*a*) for altitudes of 3.24, 1.6, and 0 km considering ionization losses in air and mesotron decay with $\epsilon_0=3\times10^{-4}$ sec. The rectangles shown in broken lines are the data of Rossi *et al.* taken at Echo Lake (3.24 km).

1×10^8 ev/c at Mount Evans can reach sea level, the spectrum as measured cannot be satisfactorily used as a basis for calculating a sea-level distribution of mesotrons. The position of the maximum, however, would be expected to occur at about 5×10^8 ev/c if mesotron production processes below 4-km altitude can be disregarded. The existing cloud-chamber experiments at sea level have tended to discriminate against such low momentum particles, producing a false maximum in the region of 10^9 ev/c.

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The author wishes to express his gratitude to Professor Marcel Schein for his many valuable suggestions in the execution of this problem, and to Professor A. H. Compton for his encouragement and helpful criticism. It is also a pleasure to acknowledge the aid of Professor Bruno Rossi of Cornell University, under whose direction the study was initiated.

[12] M. Schein and V. C. Wilson, Rev. Mod. Phys. **11**, 292 (1939); M. Schein, W. P. Jesse, and E. O. Wollan, Phys. Rev. **57**, 874 (1940); M. Schein, E. O. Wollan, and G. Groetzinger, Phys. Rev. **58**, 1027 (1940).

[13] V. H. Regener, Phys. Rev. **61**, 105 (1942).

[14] B. Rossi, K. Greisen, J. C. Stearns, D. K. Froman, and P. G. Koontz, Phys. Rev. **61**, 678 (1942).

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Optical Properties and Electronic Structure of Solid Silicon*

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The existence of an empty (conduction) band 1.5 or 2.0 volts above the highest filled band in metallic-looking semi-conductors such as silicon and certain sulfides is inferred from the optical properties of these substances. Reflectivity data of silicon are examined with the aid of the expression for the complex index of refraction as given by classical electromagnetic theory. Through use of this expression, which is checked for internal consistency, an oscillator strength of 1.6 electrons is calculated for the absorption, and a dielectric constant at low frequencies of 12.5 is computed. The Wigner-Seitz-Slater method of computing electronic energy bands in crystals is used to determine the band structure of silicon. A combination of one s, three p, and three d functions for each of the two atoms in the unit cell is made, and through use of boundary conditions of continuity of value, of normal, and of tangential derivatives, a solution is obtained for the plane $x=y$. The resulting band structure closely resembles that obtained by Kimball for the diamond, except that silicon is more nearly metallic than is the diamond. The $3s$ level of the silicon atom splits into two bands, the $3p$ level into six bands, and the $3d$ level into six bands; the two $3s$ bands and the lowest two $3p$ bands are completely filled by electrons. At the observed half-distance between nearest neighbors, the gap between the uppermost filled band and the lowest empty band is much greater than that expected from consideration of the optical data. The form of the optical absorption as expected from band structure considerations is proposed. The width of the filled bands as observed in soft x-ray emission spectra is about equal to the width of the computed bands.

I

THERE is in addition to the metals another group of substances which possesses the so-called characteristic metallic luster. In this group are the elements silicon and germanium, and many minerals, mostly sulfides, such as pyrite (fool's gold, FeS_2), molybdenite (MoS_2), galena (PbS), and stibnite (Sb_2S_3). All of these substances conduct electricity feebly at room temperature and may be classed electrically as semi-conductors. To our knowledge there are no substances which look metallic and which are not metals or semi-conductors.

The question at once arises what connection exists between metallic appearance and conductivity. It is first necessary to determine what is meant by metallic appearance. Inspection of reflectivity data[1] reveals that only metallic-looking substances such as the previously-mentioned semi-conductors have reflection coefficients above 35 percent throughout most of the visible spectrum. There are some substances such as the aniline dyes and $KMnO_4$ which reflect metallically in narrow wave-length regions; in these, the strong reflection is brought about by a definite, allowed electronic transition within the molecule or ion. Our interest, however, is in metallic reflection extending over a wide range of frequencies, over most of the visible and perhaps into the ultraviolet.

Careful examination of the equations relating absorption and reflection shows that one cannot get a reflection coefficient of 35 percent or more over a wide range except by transitions corresponding to a total electron strength of the order of unity. In metals there are enough electrons in the conduction bands and these overlapping bands are sufficiently broad to permit within the bands transitions which give sufficient reflection. It is obvious, however, that in semi-conductors the conduction electrons, which are few in number and cannot contribute appreciably to the absorption, do not play an important part in the high reflectivity of many members of this class of substances.

In semi-conductors, the metallic appearance must be due in general to the existence of a strong (i.e., $f\sim1$), wide absorption band covering the visible. This can, in the simplest manner, be ascribed to the existence of a broad, empty (conduction) band with a lower limit 12,000–15,000 wave numbers (1.5–2.0 volts) above the uppermost filled band.[2]

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[1] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. V, p. 254.

[2] Such a view has been proposed by F. Möglich and R. Rompe, Zeits. f. Physik 119, 472 (1942).

From this brief consideration of the conductivity and reflectivity of metallic-looking semiconductors, certain conclusions seem to be justified. There exists in these semi-conductors an empty (conduction) band, with a lower limit 1.5–2.0 volts above the highest filled band, and a width of several volts. Transitions into this band from the uppermost filled band are allowed, and give correspondingly strong absorption and reflection in the visible. At high temperatures, some electrons possess enough energy to go across the 1.5–2.0 volt forbidden region between the highest filled band and the empty band; these high energy electrons in the conduction band and the holes produced in the filled band by their leaving are responsible for the intrinsic conductivity of these substances. Thus the nearness of this empty band to the filled band both makes these solids intrinsic semi-conductors[3] at high temperatures, and gives them metallic appearance.

II

It is the purpose of this section to examine the refractive indices n, and the coefficients of absorption $n\kappa$, of silicon in the visible region as determined by experiment to provide quantitative evidence of the existence of a band structure as described in the first section. The experimental values of n and κ are to be used to find the oscillator strength of the band. Then, as a check, theoretical values of $n^2-n^2\kappa^2$ are to be calculated by use of an expression developed for band absorption through the classical theory of dispersion. The optical properties of silicon are also to be used to calculate the dielectric constant of silicon at low frequencies.

For a single absorption line, it can be shown[4] from the classical theory of dispersion that at the frequency ν

$$n^2(1-i\kappa)^2=1+\frac{Ne^2}{\pi m}\frac{f}{\nu_0^2-\nu^2+i\nu\nu'}, \qquad (1)$$

where N is the number of atoms per cubic centimeter, ν_0 the frequency of the absorption line, ν' a quantity measuring its width, and f the "electron number" or oscillator strength to which the strength of the line is proportional. Classically, f should be 1.

The absorption coefficient $n\kappa$ is defined so that the amplitude of light of frequency ν, after penetrating a thickness x of the material, is diminished by the factor

$$\exp\left[-\frac{2\pi\nu n\kappa x}{c}\right].$$

If, as in silicon, there is a broad absorption band instead of a single line, the relationship (1) can be used if the oscillator strength is distributed over the band; f is replaced by $(df/d\nu_0)d\nu_0$, the oscillator strength in the interval between ν_0 and $\nu_0+d\nu_0$, and the second term of the right side of (1) is integrated over the entire band. Expression (1) then becomes

$$n^2(1-i\kappa)^2=1+\frac{Ne^2}{\pi m}\int\frac{1}{\nu_0^2-\nu^2+i\nu\nu'}\frac{df}{d\nu_0}d\nu_0. \qquad (2)$$

If the real and imaginary parts of (2) are separated, the following equation is obtained for the imaginary part:

$$i2n^2\kappa=i\frac{Ne^2}{\pi m}\int\frac{\nu'\nu}{(\nu_0^2-\nu^2)^2+\nu^2\nu'^2}\frac{df}{d\nu_0}d\nu_0. \qquad (3)$$

The quantity ν', which measures the width of the absorption due to an oscillator element of strength df at a given ν_0 and arises from radiation damping, can be assumed to be vanishingly small, since the radiation damping can be shown to be negligible. The limit, then, of (3) can be taken as ν' approaches zero, and the result can be solved for $df/d\nu_0$. In this way it is found that at the frequency ν_0 the value of $df/d\nu_0$ is[5] given by

$$\frac{df}{d\nu_0}=\frac{4m}{Ne^2}n^2\kappa\nu_0. \qquad (4)$$

To evaluate $df/d\nu_0$, it is necessary to have measured values of n and $n\kappa$ throughout the band. Using a method developed by Drude,[6] Pfestorf[7] has determined values of n and $n\kappa$ at intervals throughout the band. From Pfestorf's data, which are presented in Fig. 1, the values

[3] An intrinsic semi-conductor is a substance which in the pure state has a small electronic conductivity that increases greatly with rising temperature.

[4] See, for example, Slater and Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1933), p. 280.

[5] H. M. O'Bryan, J. Opt. Soc. Am. **26**, 125 (1936).

[6] P. Drude, Wied. Ann. **64**, 162 (1898).

[7] G. Pfestorf, Ann. d. Physik **81**, 925 (1926).

of $n^2\kappa$ listed in Table I and plotted in Fig. 2 were determined. From the plotted values of $n^2\kappa$ in (4), $df/d\nu_0$ was calculated at various frequencies as presented in Table II and the second curve of Fig. 2. As shown in Fig. 2, the broad absorption band lies well within the given frequency limits. In the following, the letter $\tilde{\nu}$ indicates wave numbers, and $df/d\tilde{\nu}=(1/c)(df/d\nu)$.

By integrating $(df/d\tilde{\nu})d\tilde{\nu}$ over the entire band using numerical methods, one obtains[5] an oscillator strength of 1.6. This absorption is much too strong to come from transitions to or from an impurity band. The simplest assumption is that the absorption is brought about by transitions from a full band to an empty (conduction) band of the lattice.

Attention can now be turned to the real part of (2),

$$n^2-n^2\kappa^2=1+\frac{Ne^2}{\pi m}\int\frac{(\nu_0^2-\nu^2)}{(\nu_0^2-\nu^2)^2+\nu^2\nu'^2}\frac{df}{d\nu_0}d\nu_0. \quad (5)$$

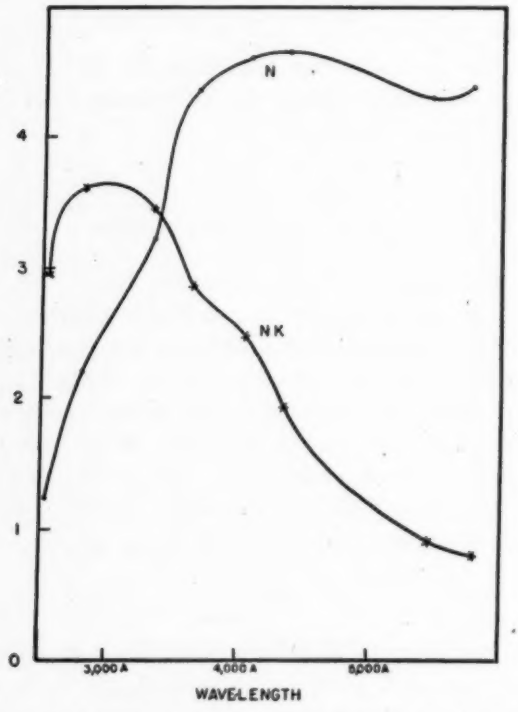

FIG. 1. Refractive index and coefficient of absorption of silicon; data of G. Pfestorf, Ann. d. Physik **81**, 925 (1926). *N* in the figure should have been *n*.

If $df/d\nu_0$ were known for all frequencies, the integral in (5) could be evaluated with the limits zero and infinity. As it is, the values of $df/d\nu_0$ have been calculated through use of optical data, so that integration can be done only over the frequencies of the visible range. However, the assumption can be made that all other absorption bands lie so far in the ultraviolet that they do not contribute to the absorption in the visible range, and add only a frequency independent quantity n_0^2-1 to the expression for $n^2-n^2\kappa^2$ for wave-lengths longer than 2500A.

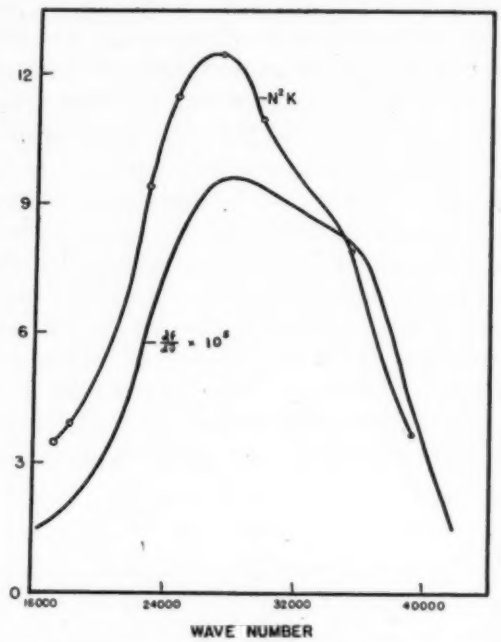

FIG. 2. Oscillator strength $df/d\tilde{\nu}$ and $n^2\kappa$ of silicon. *N* in the figure should have been *n*.

As the limit ν' approaches zero, the expression for the refractive index n and the coefficient of absorption $n\kappa$ at the wave number $\tilde{\nu}_1$ is given by

$$n^2-n^2\kappa^2=n_0^2+\frac{Ne^2}{\pi mc^2}\int\frac{1}{\tilde{\nu}^2-\tilde{\nu}_1^2}\frac{df}{d\tilde{\nu}}d\tilde{\nu}, \quad (6)$$

in which $\tilde{\nu}$ is the wave number at which the oscillator strength $(df/d\tilde{\nu})d\tilde{\nu}$ is located, and

$$\frac{Ne^2}{\pi mc^2}\frac{1}{\tilde{\nu}^2-\tilde{\nu}_1^2}\frac{df}{d\tilde{\nu}}d\tilde{\nu} \quad (7)$$

is the contribution this oscillator strength makes to $n^2-n^2\kappa^2$ at $\tilde{\nu}_1$; the integration is performed over the visible region using graphical methods. The values of this integral for various wave numbers $\tilde{\nu}_1$ are listed in the fourth line of Table III; in the third line are given the values of $n^2-n^2\kappa^2$ determined by experiment. The last line

is the difference between the third and fourth lines, and should be equal to n_0^2. The data are plotted in Fig. 3.

The values of the differences are all positive, as they must be if they are to represent n_0^2; they show no reasonable trend. It can be assumed that the variations are due to experimental uncertainties, and as the value of n_0^2 the arithmetical average may be taken: $n_0^2=2.6$.

From these data it is possible to calculate the dielectric constant. The electrical properties of a material like silicon depend on the bound electrons and on the free or conduction electrons. For the dielectric constant as used in space charge formulae, the contribution of the conduction electrons is to be omitted, as the contribution of these electrons to the electric field has already been taken into account in the space charge, and would be counted twice if it were also included in the dielectric constant.

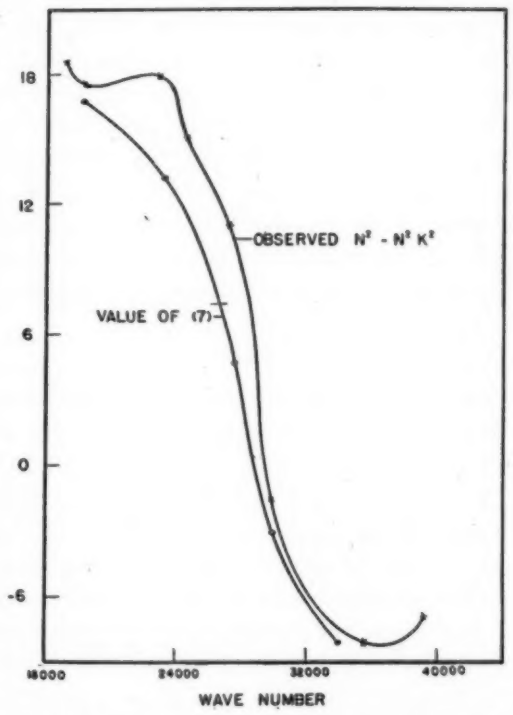

FIG. 3. Observed $n^2-n^2\kappa^2$ and computed value of integral (7). N in the figure should have been n.

If the refractive index n is known at zero frequency, the dielectric constant ϵ can be found from

$$\lim_{\nu\to 0} n^2=\epsilon.$$

Placing ν_1 in (6) equal to zero, one finds that the expression for the dielectric constant at low frequency becomes

$$\epsilon=n_0^2+\frac{Ne^2}{\pi mc^2}\int\frac{1}{\bar{\nu}^2}\frac{df}{d\bar{\nu}}d\bar{\nu}. \tag{8}$$

Graphical integration of the second term leads to a value of 9.9, and therefore to

$$\epsilon=12.5.$$

Apart from the uncertainty of the optical data, which is difficult to judge, the accuracy of ϵ is estimated to be ± 0.5.

In the preceding, any influence of the conduction electrons on the optical properties has been completely omitted. If these are completely free, their contribution to n^2 would be $-(N_1e^2)/(\pi mc^2)1/\bar{\nu}^2$. With $N_1=6\times 10^{19}$, $\bar{\nu}=20{,}000$, the value of the above is -0.024, which is below experimental accuracy.

III

Quantitative investigation of the electronic structure of solids has been confined largely to studies of the structure of metallic and ionic crystals. The atoms which form valence crystals have so many outer electrons which are affected appreciably by entrance into the crystalline state that computation involved in determining approximately the electronic structure becomes difficult. As a consequence of this difficulty, the work on valence crystals has not been extensive, and no band structure studies of the silicon crystal have been made. In this section, a method of quantum mechanical approximation is to be used to see if the origin of the observed absorption of silicon can be found in the band structure as given by this approximation.

A method of obtaining approximate solutions of the Schrödinger equation which has been used successfully for valence crystals is the well-known method developed by Wigner and Seitz[8] and extended by Slater.[9] Wigner and Seitz observed that in a crystal having a high degree of rotational symmetry relative to the nucleus, the potential field acting on an electron in the neighborhood of the nucleus is spherically sym-

[8] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

[9] J. C. Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 209 (1934).

metrical to a good approximation. As in the case of isolated atoms, the Schrödinger equation can be solved by separation of variables and by numerical integration of the radial equation for the radial function. Each nucleus in the lattice can be considered to be the center of a roughly spherical cell which is bounded by planes so that together with the cells about other nuclei it will fill all space. The wave function for the entire lattice can be obtained by solving the Schrödinger equation in one of the cells, subject to certain conditions at the cell boundary. This method was used in the determination of the electronic energy bands of the diamond by Kimball[10] and by Hund[11] and Mrowka.[12]

The structure of the silicon crystal like that of the diamond is face-centered cubic with two atoms in the unit cell; the edge of the unit cell is 5.42A in length,[13] and the distance between nearest neighbors is 2.35A or 4.44 Bohr radii. As in the work of Kimball,[10] one atom of the unit cell is considered to be at the origin of a Cartesian coordinate system and the other at the point (a, a, a); the entire lattice may be formed by translating these atoms of the unit cell by vectors of the form $n_1\mathbf{v}_1+n_2\mathbf{v}_2+n_3\mathbf{v}_3$ where the components of $\mathbf{v}_1$ are 0, $2a$, $2a$; those of $\mathbf{v}_2$ are $2a$, 0, $2a$; and those of $\mathbf{v}_3$ are $2a$, $2a$, 0; and where n_1, n_2, and n_3 are arbitrary integers.

The Wigner-Seitz polyhedron for silicon is made up of a tetrahedron formed by the planes bisecting perpendicularly the lines joining the atom to its four nearest neighbors. The corners of this tetrahedron are cut off by the planes bisecting perpendicularly the twelve lines to the next nearest neighbors. The result is a sixteen-sided polyhedron having four large hexagonal faces.[14]

As there are two atoms in the unit cell of silicon, it is necessary to consider the behavior of wave functions in two Wigner-Seitz polyhedra simultaneously. The polyhedra surrounding the two atoms of the unit cell are identical, but are oppositely oriented. The wave function can be considered to be made up of an even part U^g and an odd part U^u. The even part U^g remains unchanged in sign in going from the midpoint of a hexagonal face of one polyhedron to the midpoint of the diametrically oppositely oriented face of an adjacent polyhedron; the sign of the function and the orientation of the face in each case are determined using a coordinate system having its origin at the center of the polyhedron being used. The odd part U^u changes sign in such translations. For convenience, the wave function U is written in the form

$$U=U^g+iU^u.$$

In the study of the electronic structure of the diamond, it was necessary to consider only the L-shell electrons in which only s and p states exist. A combination of eight wave functions and the eight simple boundary conditions of continuity of the wave function and its normal derivative at the four pairs of midpoints sufficed. In silicon, the electrons of interest are in the M shell, and it can be expected that d states will deserve consideration.

The geometry of the Wigner-Seitz polyhedron for the diamond lattice is such that only the centers of the four hexagonal faces can be used for application of the boundary conditions. Any combination of wave functions which is to take into consideration the s, p, and d levels must contain more than eight functions, the maximum

TABLE I. Experimental data.

λ in A	5780	5460	4360	4060	3660	3350	2810	2540
$\tilde{\nu}$	17300	18300	22930	24630	27320	29850	35600	39370
$n^2\kappa$	3.5	3.9	9.4	11.5	12.5	11.0	7.9	3.7

TABLE II. Oscillator strength.

$\tilde{\nu}$	16000	18000	20000	22000	24000	26000	28000	30000	32000
$\frac{df}{d\tilde{\nu}}\times10^4$	15	20	30	50	75	90	96	93	89
$\tilde{\nu}$	36000	38000	40000	41700					
$\frac{df}{d\tilde{\nu}}\times10^4$	78	59	37	15					

TABLE III. Comparison of experimental and theoretical data for $n^2-n^2\kappa^2$.

λ	5451	4286	3623	3331	2998
$\tilde{\nu}_1$	18300	23300	27600	30000	33300
$n^2-n^2\kappa^2$	17.5	17.6	10.0	−1.5	−6.8
Integral (7)	16.8	13.3	4.7	−3.1	−8.1
Difference	0.7	4.3	5.3	1.6	1.3

[10] G. E. Kimball, J. Chem. Phys. **3**, 560 (1935). We often use Kimball's notation.
[11] F. Hund, Physik. Zeits. **36**, 888 (1935).
[12] F. Hund and B. Mrowka, Ber. d. Sachs. Akad. d. Wiss. math-phys. Kl. **87**, 185 (1935).
[13] H. Küstner and H. Remy, Physik. Zeits. **24**, 25 (1923).
[14] A drawing of this polyhedron is presented in reference 10.

that can be determined by use of the usual boundary conditions. It is necessary, therefore, to introduce additional boundary conditions.

It was first attempted to include all five $3d$ levels in the combination of wave function. Accordingly, the odd and the even part of the total wave function were made up of the $3s$ function, the three $3p$ functions, the five $3d$ functions, and one $4f$ function. As there were four points in each polyhedron at which the boundary conditions could be applied, it was thought that the number of terms in the total wave function must be a multiple of four; it was for this reason that an f function was added to the odd and even parts of the total wave function to give twenty coefficients. Five boundary conditions at each of the four joining points were sought. The boundary conditions selected were the usual conditions of continuity of the value and of the first normal derivative of the functions; the new conditions were the continuity of the second normal derivative, and the continuity of the two components of the tangential derivative.[15] Solutions of the twenty simultaneous equations were sought for the condition[10] $M=L=0$. It was found that the equations were not all independent and would not give twenty solutions. No way of avoiding the difficulty was found, and it was decided to abandon the attempt to use twenty functions.

A revision of the boundary conditions was then made in an attempt to get as many independent equations as there were functions. The revised boundary conditions were the continuity of the function and of first, second, and third normal derivatives. The total wave function was as before, except that only the three $3d$ functions having the surface harmonics xy/r^2, yz/r^2, xz/r^2, were used. Independent solutions were found for the condition $M=L=0$, but when numerical values were calculated, the solutions appeared completely unreasonable. It appears that the continuity of normal derivatives of order higher than the first are not satisfactory boundary conditions.

The conditions of continuity of the second and third normal derivatives were then replaced by the continuity of the two components of the tangential derivative. The same combination of wave functions was used as in the preceding case. The first attempt at solution was made for the condition $L=M=0$, but it again appeared that there were too few independent equations to determine the s, p, and d function coefficients. However, when the equations were examined for the condition which Kimball[10] uses, $K=L$, it was found that fourteen unknowns could be determined from the sixteen equations. Accordingly, the $4f$ functions in the odd and in the even part of the total function were dropped, and the values of the coefficients of the remaining fourteen s, p, and d functions were determined from the sixteen equations. As this procedure was used as the basis of the numerical work which follows, the solution is given in detail.

The boundary conditions of continuity of the value of the wave function, of the normal derivative, and of the two components of the tangential derivative may be stated more explicitly as:[16]

[15] Continuity of the tangential derivatives was suggested as a boundary condition by W. Shockley, Phys. Rev. **52**, 866 (1937).

[16] The form of the differential operator in the expressions giving the components of the tangential derivative may be developed as follows: at the midpoint x_1, y_1, z_1 of a hexagonal face of the polyhedron let there be a normal vector with direction cosines x_1/r_1, y_1/r_1, and z_1/r_1, where r_1 is the distance to the origin, which is at the center of the polyhedron. The normal vector to the midpoint of the face will pass through the origin. In the plane of the face let there be a second vector through the midpoint with components dx, dy, and dz and direction cosines dx/ds, dy/ds, and dz/ds, where $ds=(dx^2+dy^2+dz^2)^{\frac{1}{2}}$. Then from the familiar relationship

$$x_1/r_1\ dx/ds+y_1/r_1\ dy/ds+z_1/r_1\ dz/ds=0 \qquad \text{(A)}$$

it follows that

$$dz=-\frac{x_1dx+y_1dy}{z_1}. \qquad \text{(B)}$$

The total differential of $F(x, y, z)$ at x_1, y_1, z_1 is

$$dF=\frac{\partial F}{\partial x}dx+\frac{\partial F}{\partial y}dy+\frac{\partial F}{\partial z}dz. \qquad \text{(C)}$$

Using (B), we may then express the tangential differential as

$$dF=\left(\frac{\partial F}{\partial x}-\frac{x_1}{z_1}\frac{\partial F}{\partial z}\right)dx+\left(\frac{\partial F}{\partial y}-\frac{y_1}{z_1}\frac{\partial F}{\partial z}\right)dy. \qquad \text{(D)}$$

The wave functions listed in Table IV involve x, y, z, and r

$$F(x, y, z)=\psi(x, y, z, r)$$

where $r=(x^2+y^2+z^2)^{\frac{1}{2}}$. The partial derivatives of the wave function then are:

$$\left(\frac{\partial F}{\partial x}\right)=\left[\frac{\partial \psi}{\partial x}\right]_{y,z,r}+\frac{x}{r}\left[\frac{\partial \psi}{\partial r}\right]_{x,y,z}, \qquad \text{(E)}$$

$$\left(\frac{\partial F}{\partial y}\right)=\left[\frac{\partial \psi}{\partial y}\right]_{x,z,r}+\frac{y}{r}\left[\frac{\partial \psi}{\partial r}\right]_{x,y,z}, \qquad \text{(F)}$$

$$\left(\frac{\partial F}{\partial z}\right)=\left[\frac{\partial \psi}{\partial z}\right]_{x,y,r}+\frac{z}{r}\left[\frac{\partial \psi}{\partial r}\right]_{x,y,z}. \qquad \text{(G)}$$

The differential quotients enclosed in square brackets [ ] refer to differentiation of the variable as it appears

$$U^v+iU^u=e^{i(\mathbf{k}\cdot\mathbf{V})}(U^v+iU^u), \tag{9a}$$

$$U'^v+iU'^u=-e^{i(\mathbf{k}\cdot\mathbf{V})}(U'^v+iU'^u), \tag{9b}$$

$$\left(\left[\frac{\partial}{\partial x}\right]-\frac{x_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)(U^v+iU^u)$$

$$=-e^{i(\mathbf{k}\cdot\mathbf{V})}\left(\left[\frac{\partial}{\partial x}\right]-\frac{x_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)(U^v+iU^u), \tag{9c}$$

$$\left(\left[\frac{\partial}{\partial y}\right]-\frac{y_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)(U^v+iU^u)$$

$$=-e^{i(\mathbf{k}\cdot\mathbf{V})}\left(\left[\frac{\partial}{dy}\right]-\frac{y_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)(U^v+iU^u). \tag{9d}$$

In the boundary conditions (9c) and (9d), the differentiation set in square brackets [ ] involves only the variable indicated as it appears explicitly in the function operated upon; r is considered as though it were independent of x, y, and z.

In the above, $\mathbf{k}$ is the wave number vector, and $\mathbf{V}$ is the translational vector from the midpoint of one hexagonal face to the midpoint of the diametrically oppositely oriented hexagonal face of an adjacent polyhedron. By combining terms, Eqs. (9) reduce to:

$$\frac{\left(\left[\frac{\partial}{\partial x}\right]-\frac{x_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)U^v}{\left(\left[\frac{\partial}{\partial x}\right]-\frac{x_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)U^u}=\frac{\left(\left[\frac{\partial}{\partial y}\right]-\frac{y_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)U^v}{\left(\left[\frac{\partial}{\partial y}\right]-\frac{y_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right)U^u}$$

$$=-\frac{U'^v}{U'^u}=\frac{U^u}{U^v}=\tan\frac{\mathbf{k}\cdot\mathbf{V}}{2}. \tag{10}$$

The joining points of the polyhedron about the atom at 0, 0, 0 are: $P_1=(a/2, a/2, a/2)$, $P_2=(a/2, -a/2, -a/2)$, $P_3=(-a/2, a/2, -a/2)$, and $P_4=(-a/2, -a/2, a/2)$. For the polyhedron about the atom at (a, a, a) the joining points are

$P_5=(-a'/2, -a'/2, -a'/2)$ or $(a/2, a/2, a/2)$,
$P_6=(-a'/2, a'/2, a'/2)$ or $(a/2, 3a/2, 3a/2)$,
$P_7=(a'/2, -a'/2, a'/2)$ or $(3a/2, a/2, 3a/2)$,
and
$P_8=(a'/2, a'/2, -a'/2)$ or $(3a/2, 3a/2, a/2)$.

TABLE IV. Values of independent wave functions.

Wave function	Value in polyhedron about (0, 0,0)	Value in polyhedron about (a, a, a)
ψ_1	$S(r)$	$-S(r')$
ψ_2	$\sqrt{3}(x/r)P(r)$	$\sqrt{3}(x'/r')P(r')$
ψ_3	$\sqrt{3}(y/r)P(r)$	$\sqrt{3}(y'/r')P(r')$
ψ_4	$\sqrt{3}(z/r)P(r)$	$\sqrt{3}(z'/r')P(r')$
ψ_5	$3(xy/r^2)D(r)$	$-3(x'y'/r'^2)D(r')$
ψ_6	$3(yz/r^2)D(r)$	$-3(y'z'/r'^2)D(r')$
ψ_7	$3(xz/r^2)D(r)$	$-3(x'z'/r'^2)D(r')$
ψ_8	$S(r)$	$S(r')$
ψ_9	$\sqrt{3}(x/r)P(r)$	$-\sqrt{3}(x'/r')P(r')$
ψ_{10}	$\sqrt{3}(y/r)P(r)$	$-\sqrt{3}(y'/r')P(r')$
ψ_{11}	$\sqrt{3}(z/r)P(r)$	$-\sqrt{3}(z'/r')P(r')$
ψ_{12}	$3(xy/r^2)D(r)$	$3(x'y'/r'^2)D(r')$
ψ_{13}	$3(yz/r^2)D(r)$	$3(y'z'/r'^2)D(r')$
ψ_{14}	$3(xz/r^2)D(r)$	$3(x'z'/r'^2)D(r')$

In the above, the primed quantities refer to a coordinate system with origin at a, a, a and the unprimed quantities to a system with origin at 0, 0, 0. If the boundary conditions are applied to these two adjacent cells, the midpoints of the oppositely oriented faces and the translational vectors $\mathbf{V}$ involved are: P_1 and P_5 with $\mathbf{V}\doteq 0$ (the faces coincide); P_2 and P_6 with $\mathbf{V}=\mathbf{v}_1$ (components 0, 2a, 2a); P_3 and P_7 with $\mathbf{V}=\mathbf{v}_2$ $(2a, 0, 2a)$; and P_4 and P_8 with $\mathbf{V}=\mathbf{v}_3$ $(2a, 2a, 0)$.

To satisfy the boundary conditions at the midpoints, the wave equation

$$U=ia_1\psi_1+ia_2\psi_2+ia_3\psi_3+ia_4\psi_4+ia_5\psi_5$$
$$+ia_6\psi_6+ia_7\psi_7+b_1\psi_8+b_2\psi_9+b_3\psi_{10}$$
$$+b_4\psi_{11}+b_5\psi_{12}+b_6\psi_{13}+b_7\psi_{14}$$

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explicitly in the function operated upon, with no regard to the dependence of r on x, y, z.

On substitution of (E), (F), and (G) in (D), the tangential differential at the point x_1, y_1, z_1, takes the form

$$dF=\left(\left[\frac{\partial\psi}{\partial x}\right]+\frac{x_1}{r_1}\left[\frac{\partial\psi}{\partial r}\right]-\frac{x_1}{z_1}\left[\frac{\partial\psi}{\partial z}\right]-\frac{z_1}{r_1}\frac{x_1}{z_1}\left[\frac{\partial\psi}{\partial r}\right]\right)dx$$
$$+\left(\left[\frac{\partial\psi}{\partial y}\right]+\frac{y_1}{r_1}\left[\frac{\partial\psi}{\partial r}\right]-\frac{y_1}{z_1}\left[\frac{\partial\psi}{\partial z}\right]-\frac{z_1}{r_1}\frac{y_1}{z_1}\left[\frac{\partial\psi}{\partial r}\right]\right)dy. \tag{H}$$

When the expressions by which dx and dy are multiplied fulfill the condition of continuity at a face of the polyhedron, the tangential derivative is continuous in any direction and the function is continuous not only at the midpoint but in its neighborhood. For want of a better name, the coefficients of dx and dy are referred to in the text as the components of the tangential derivative.

As can be seen from (H), the operators involved in these tangential boundary conditions are

$$\left(\left[\frac{\partial}{\partial x}\right]-\frac{x_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right) \tag{I}$$

and

$$\left(\left[\frac{\partial}{\partial y}\right]-\frac{y_1}{z_1}\left[\frac{\partial}{\partial z}\right]\right). \tag{J}$$

Thus the so-called components of the tangential derivative do not involve explicitly differentiation of $\psi(x, y, z, r)$ with respect to r.

was built up of the fourteen independent functions whose values in the two polyhedra are listed in Table IV.

In Table IV, $S(r)$, $P(r)$, and $D(r)$ are the radial parts of the wave functions; x, y, and z are Cartesian coordinates with origin at (0, 0, 0) and r is the distance from (0, 0, 0); x', y', z', and r' are similarly related to the point (a, a, a).

The equations obtained from the boundary conditions are:

$$s(a_1)+p(a_2+a_3+a_4)+d(a_5+a_6+a_7)=0, \quad (11a)$$

$$s(a_1)+p(a_2-a_3-a_4)+d(-a_5+a_6-a_7)+K[s(b_1)+p(b_2-b_3-b_4)+d(-b_5+b_6-b_7)]=0, \quad (11b)$$

$$s(a_1)+p(-a_2+a_3-a_4)+d(-a_5-a_6+a_7)+L[s(b_1)+p(-b_2+b_3-b_4)+d(-b_5-b_6+b_7)]=0, \quad (11c)$$

$$s(a_1)+p(-a_2-a_3+a_4)+d(a_5-a_6-a_7)+M[s(b_1)+p(-b_2-b_3+b_4)+d(b_5-b_6-b_7)]=0, \quad (11d)$$

$$s'(b_1)+p'(b_2+b_3+b_4)+d'(b_5+b_6+b_7)=0, \quad (11e)$$

$$-K[s'(a_1)+p'(a_2-a_3-a_4)+d'(-a_5+a_6-a_7)]+s'(b_1)+p'(b_2-b_3-b_4)+d'(-b_5+b_6-b_7)=0, \quad (11f)$$

$$-L[s'(a_1)+p'(-a_2+a_3-a_4)+d'(-a_5-a_6+a_7)]+s'(b_1)+p'(-b_2+b_3-b_4)+d'(-b_5-b_6+b_7)=0, \quad (11g)$$

$$-M[s'(a_1)+p'(-a_2-a_3+a_4)+d'(a_5-a_6-a_7)]+s'(b_1)+p'(-b_2-b_3+b_4)+d'(b_5-b_6-b_7)=0, \quad (11h)$$

$$p(b_2-b_4)+d(b_5-b_6)=0, \quad (11i)$$

$$-K[p(a_2+a_4)+d(-a_5-a_6)]+p(b_2+b_4)+d(-b_5-b_6)=0, \quad (11j)$$

$$-L[p(a_2-a_4)+d(a_5-a_6)]+p(b_2-b_4)+d(b_5-b_6)=0, \quad (11k)$$

$$-M[p(a_2+a_4)+d(-a_5-a_6)]+p(b_2+b_4)+d(-b_5-b_6)=0, \quad (11l)$$

$$p(b_3-b_4)+d(b_5-b_7)=0, \quad (11m)$$

$$-K[p(a_3-a_4)+d(a_5-a_7)]+p(b_3-b_4)+d(b_5-b_7)=0, \quad (11n)$$

$$-L[p(a_3+a_4)+d(-a_5-a_7)]+p(b_3+b_4)+d(-b_5-b_7)=0, \quad (11o)$$

$$-M[p(a_3+a_4)+d(-a_5-a_7)]+p(b_3+b_4)+d(-b_5-b_7)=0. \quad (11p)$$

In Eqs. (11) and (18), the a's and b's are factors, not arguments.

In the above equations,

$$s=S(R), \quad s'=(dS/dr)_{r=R},$$
$$p=P(R), \quad p'=(dP/dr)_{r=R},$$
$$d=D(R), \quad d'=(dD/dr)_{r=R},$$

where R is the distance from the center of the polyhedron to the midpoint of the hexagonal face. The definitions of K, L, and M are

$$K=\tan(\mathbf{k}\cdot\mathbf{v}_1/2), \quad L=\tan(\mathbf{k}\cdot\mathbf{v}_2/2),$$

and $M=\tan(\mathbf{k}\cdot\mathbf{v}_3/2)$.

Equations (11a) to (11d) express the condition of continuity of the wave function itself at the four selected pairs of points, (11e) to (11h) that of the continuity of the normal derivative, (11i) to (11l) that of the "x component" of the tangential derivative, and (11m) to (11p) that of the "y component."

To make solution of these equations feasible, propagation of electron waves is restricted to the plane $x=y$, i.e., $\mathbf{k}_x=0$. Then, as in Kimball's solution,[10] $K=L$. The sixteen simultaneous equations can be broken into two sets of eight equations. The first set, obtained from the boundary conditions of continuity of the value and of the normal derivative, contains s, p, d, s', p', and d', and the fourteen constants. The second set of eight equations, obtained from the boundary conditions of continuity of the components of the tangential derivative, contains only p and d and the twelve constants associated with p and d. The equations of this latter set are used to obtain the coefficients of d in terms of p/d and the coefficients of p; then the coefficients of d are eliminated from the first set.

As the first step in this procedure, Eq. (11l) was subtracted from (11j) with the result

$$(M-K)[p(a_2+a_4)-d(a_5+a_6)]=0$$

or

$$pa_2-da_6=-(pa_4-da_5).$$

By subtracting (11i) from (11k) we find that

$$pa_2-da_6=pa_4-da_5.$$

Obviously, then,

$$pa_2-da_6=pa_4-da_5=0$$

from which

$$pa_2=da_6 \tag{12}$$

and

$$pa_4=da_5. \tag{13}$$

By use of the above relationships in (11j) and (11k) it is found through similar reasoning that

$$pb_2=db_6 \tag{14}$$

and

$$pb_4=db_5. \tag{15}$$

In the same way, (11m) and (11n) give the relationships

$$pb_3=db_7 \tag{16}$$

and

$$pa_3=da_7. \tag{17}$$

Equations (11o) and (11p) are identically fulfilled.

The first set of eight equations was then simplified by substituting for the coefficients of d their values in terms of the coefficients of p. These equations become

$$s(a_1)+2p(a_2+a_3+a_4) \tag{18a}$$

$$s(a_1)+2p(a_2-a_3-a_4)+K[s(b_1)+2p(b_2-b_3-b_4)]=0, \tag{18b}$$

$$s(a_1)+2p(-a_2+a_3-a_4)+L[s(b_1)+2p(-b_2+b_3-b_4)]=0, \tag{18c}$$

$$s(a_1)+2p(-a_2-a_3+a_4)+M[s(b_1)+2p(-b_2-b_3+b_4)]=0, \tag{18d}$$

$$s'(b_1)+\left(p'+\frac{pd'}{d}\right)(b_2+b_3+b_4)=0, \tag{18e}$$

$$-K\left[s'(a_1)+\left(p'+\frac{pd'}{d}\right)(a_2-a_3-a_4)\right]+s'(b_1)+\left(p'+\frac{pd'}{d}\right)(b_2-b_3-b_4)=0, \tag{18f}$$

$$-L\left[s'(a_1)+\left(p'+\frac{pd'}{d}\right)(-a_2+a_3-a_4)\right]+s'(b_1)+\left(p'+\frac{pd'}{d}\right)(-b_2+b_3-b_4)=0, \tag{18g}$$

$$-M\left[s'(a_1)+\left(p'+\frac{pd'}{d}\right)(-a_2-a_3+a_4)\right]+s'(b_1)+\left(p'+\frac{pd'}{d}\right)(-b_2-b_3+b_4)=0. \tag{18h}$$

Up to here, no use has been made of the restriction $K=L$. These equations are identical with Eqs. (1a) to (1h) in Kimball's paper[10] on the diamond, with p and p' of Kimball's equations replaced, respectively, with $2p$ and $p'+(pd')/d$. Kimball has obtained a solution of these equations

$$\omega=\frac{-(10K^2M^2+8K^2+8KM+10M^2+16)}{3K^2M^2+4K^2-4KM+3M^2}, \tag{19}$$

where $\omega=(\mu^2+1)/\mu$ and $\mu=sp'/s'p$. This solution can be used for Eqs. (18) if μ is redefined as

$$\mu=\frac{s(p'/p+d'/d)}{2s'}. \tag{20}$$

Through use of Eq. (19), ω can be evaluated directly from $\mathbf{k}$, and since ω is known through numerical computation as a function of E, the relationship of E and $\mathbf{k}$ can be determined.

Determination of E from $\mathbf{k}$ involves the evaluation of s, s', p, p', d, and d'. These values were obtained through numerical integration of the Schrödinger equation; the details of this computation are given in Appendix I. A plot of ω against μ gives a double-branch curve only the negative branch of which, as inspection of Eq. (19) will show, need be considered. As μ approaches 0 and $-\infty$, ω approaches $-\infty$ as a limit; this corresponds to $K=M=0$. The values of s, s', p, p', d, and d' which will make $|\omega|=\infty$ form the limits of the bands at which $\mathbf{k}=0$; these values are $s=0$, $s'=0$, $p'/p+d'/d=0$, $p=0$, and $d=0$. The negative branch of ω has a maximum of -2 when $\mu=-1$, which corresponds to the place in the band at which k has the highest value. At $\mu=-1$, $s/s'+2/(p'/p+d'/d)=0$.

When Eq. (19) is used in the process of finding E as a function of $\mathbf{k}$, it is found that to each value of $\mathbf{k}$ there are six values of E. As shown in Fig. 4, at the observed half-internuclear distance the lowest of these values lies in the region between curve (I) $s'=0$, $(\mathbf{k}=0)$, and (II) the lowest

branch of $s/s'+2/(p'/p+d'/d)=0$, $(\mathbf{k}=\infty)$; the second value is in the region bounded by this latter curve and (IV) the lower branch of $p'/p+d'/d=0$, $(k=0)$; the region of the third value is bounded by (III) $s=0$, and by (V) the middle branch of $s/s'+2/(p'/p+d'/d)=0$, $(\mathbf{k}=\infty)$; the fourth value is in the region bounded by (V), and by (VI) $p=0$, $(\mathbf{k}=0)$; the regions of the fifth and sixth values are not shown in Fig. 4 since they are of such high energy that they are of little interest. The region of the fifth value lies between the upper branch of $p'/p+d'/d=0$, $(\mathbf{k}=0)$, and the highest of the three branches of $s/s'+2/(p'/p+d'/d)=0$ $(\mathbf{k}=\infty)$; the region of the sixth value is between this latter branch and the curve $d=0$, $(\mathbf{k}=0)$.

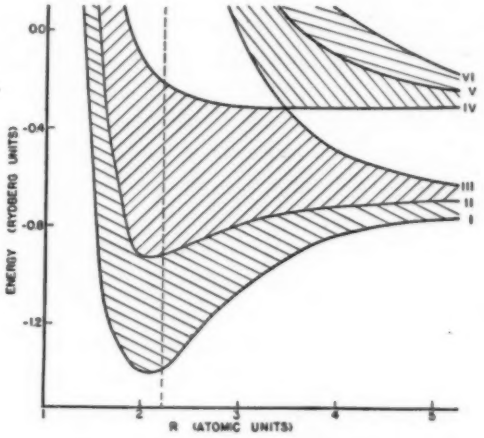

FIG. 4. Energy bands of silicon as a function of R (one-half the distance between nearest neighbors). The curves are: I, $s'=0$; II, $s/s'+2/(p'/p+d'/d)=0$; III, $s=0$; IV, (doubly degenerate) $p'/p+d'/d=0$; V, $s/s'+2/(p'/p+d'/d)=0$; VI, (doubly degenerate) $p=0$.

In addition to the above six band regions, degenerate bands arise from Eqs. (3a) and (3b) in Kimball's paper.[10] These equations may be rewritten in the form

$$2p(a_2-a_3)+K2p(b_2-b_3)=0,$$

$$-K(p'+pd'/d)(a_2-a_3)+(p'+pd'/d)(b_2-b_3)=0.$$

They are satisfied by any value of $\mathbf{k}$ if $p=0$, or if $p'+(pd')/d=0$.

The values of the coefficients were determined for the case $p=0$, and are found to be

$$a_4=[-M/(2K-M)](a_2+a_3), \tag{21a}$$

$$b_2=[K/(2K-M)][(K-M)a_2-Ka_3], \tag{21b}$$

$$b_3=[-K/(2K-M)][Ka_2-(K-M)a_3], \tag{21c}$$

$$b_4=[KM/(2K-M)][a_2+a_3]. \tag{21d}$$

For the condition $p'/p+d'/d=0$, the coefficients are

$$a_4=-(a_2+a_3), \tag{22a}$$

$$b_2=[1/(MK)][-Ka_2+(M-K)a_3], \tag{22b}$$

$$b_3=[1/(MK)][(M-K)a_2-Ka_3], \tag{22c}$$

$$b_4=[1/K][a_2+a_3]. \tag{22d}$$

Thus two bands of zero width follow $p=0$, and two follow each of the two branches of $p'/p+d'/d=0$.

Two additional bands of zero width can be shown to follow the curve $d=0$. To determine this it is necessary to go back to the original conditions, and to examine them for this special case. If $d=0$, $p\neq 0$, it follows from relationships (11j) to (11p) derived from the continuity of the components of the tangential derivative that $a_2=a_3=a_4=b_2=b_3=b_4=0$. By use of these values in Eqs. (11a) and (11b), we find that $sa_1=0$, and $sb_1=0$; it follows that Eqs. (11c) to (11h) may be written as

$$d'(b_5+b_6+b_7)=0, \tag{23a}$$

$$-Kd'(-a_5+a_6-a_7)+d'(-b_5+b_6-b_7)=0, \tag{23b}$$

$$-Kd'(-a_5-a_6+a_7)+d'(-b_5-b_6+b_7)=0, \tag{23c}$$

$$-Md'(a_5-a_6-a_7)+d'(b_5-b_6-b_7)=0. \tag{23d}$$

Through simple algebra it may be shown from the above that

$$b_5=-(b_6+b_7), \tag{24a}$$

$$a_5=-(1/K)(b_6+b_7), \tag{24b}$$

$$a_6=-(1/2)[(1/K-2/M)(b_6+b_7)-(1/K)(b_6-b_7)], \tag{24c}$$

$$a_7=-(1/2)[(1/K-2/M)(b_6+b_7)+(1/K)(b_6-b_7)]. \tag{24d}$$

Thus it is possible to express all but two of the unknowns in terms of the others. From this it is seen that two bands of zero width are contained in the solution $d=0$.

Certain essential features of silicon can be understood qualitatively through study of Fig. 4. One would expect that at absolute zero the eight

electrons of the unit cell, four electrons to the atom, at the observed half-internuclear distance would fill completely the two lower bands and the two degenerate bands following curve IV. With no partially empty bands, silicon would not conduct electricity at lower temperatures.

That silicon just misses being a metal can also be seen in Fig. 4. At half-internuclear distances greater than 3.5, the two degenerate bands following curve IV touch the empty bands bounded by curves IV and VI. If silicon could exist at these increased half-internuclear distances, it would be a metal of good conductivity.

To determine the extent by which the band structure obtained by including consideration of three $3d$ functions, besides giving a d band of high energy, differed from the band structure obtained by using Kimball's solutions[10] in which no d functions were considered, the values of s, s', p, and p' calculated for silicon were used in Kimball's solutions. The results are shown in Fig. 5 as a plot of energy against half-distance between nearest neighbors. Kimball's solution $p'=0$ (curve IV of Fig. 5) replaces $p'/p+d'/d=0$ (curve IV of Fig. 4). The curve $p'=0$ is significantly lower than the curve $p'/p+d'/d=0$; at the observed half-internuclear distance, the energy difference of curves III and IV is 0.44 Rydberg units more in Fig. 5 than it is in Fig. 4.

Experimental information about the width of the M band of silicon is furnished by the soft x-ray emission spectra obtained for silicon by O'Bryan and Skinner.[17] The emission bands represent transitions from the broad M band to a relatively sharp L level, so that the width of the observed x-ray band is approximately equal to the energy width of the M band. The width of the x-ray band of silicon was found to be 19.2 ± 2.5 volts. The width of the band of Fig. 4 at the observed half-internuclear distance is about 16 volts; that of Fig. 5 is about 9.5 volts. The photometer curve of the x-ray band is smooth with a gradual rise and a more abrupt fall, indicating more transitions of high energy electrons of the M shell than of low energy electrons. One might expect that there would be a well-defined large peak toward the high energy end

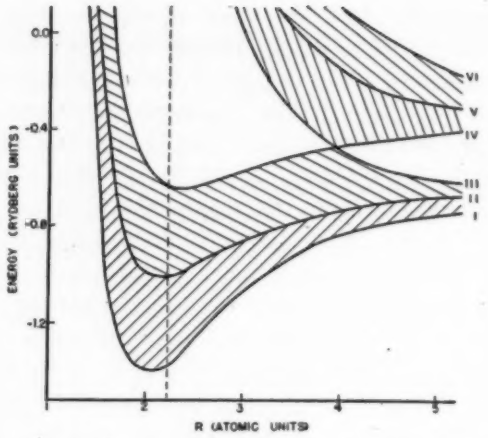

FIG. 5. Energy bands of silicon as a function of R (one-half the distance between nearest neighbors), using Kimball's solution for the diamond lattice. The curves are: I, $s'=0$; II, $s/s'+p/p'=0$; III, $s=0$; IV (doubly degenerate), $p'=0$; V, $s/s'+p/p'=0$; VI (doubly degenerate) $p=0$.

of the x-ray band corresponding to transitions from the narrow bands (of zero width in our approximation) following curve IV of Fig. 4. It has been shown,[18] however, that the optical transition probability is not simply related to the level density in a given energy region.

Unfortunately the results expressed in Fig. 4 do not agree quantitatively with the conclusions drawn in the first part from the optical properties and the intrinsic conductivity. The optical properties lead us to expect an energy gap between the full band and the lower conduction band of not more than 1.5 to 2.0 volts, or about 0.15 Rydberg unit; the conductivity measurements point in the same direction. The energy gap in Fig. 4, as estimated by extrapolation, is at least 0.8 Rydberg unit.

It is interesting to compare this energy gap with that for the diamond and that obtained for silicon using Kimball's solutions (Fig. 5). For diamond ($2s$ and $2p$ orbits) Kimball[10] has found a gap of 4 or 5 Rydberg units, which is also much too high, since diamond absorbs at about 1800A, and should have a gap of about 0.5 Rydberg unit. Figure 5, which takes only $3s$ and $3p$ orbits into account, gives an estimated energy gap for silicon of about 1.3 Rydberg units. The introduction of the $3d$ orbits brings this down to about 0.8 unit.

[17] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

[18] H. Jones, N. F. Mott, and H. W. B. Skinner, Phys. Rev. **45**, 379 (1934).

This disagreement of the calculated energy gaps with experiment is probably explained by Shockley's statement[19] that the method of Wigner and Seitz is fairly good for the ground state, i.e., the full bands—in Fig. 4 the region between curves I, II, and IV—but leads to completely erroneous results for excited states, i.e., the region between curves III, V, and VI. It must be expected that in reality curve III lies much lower on the left and is much flatter.

The average electron energy for a given half-internuclear distance may be computed from Figs. 4 and 5 by means of[20]

$$E_{Av}=0.625E_{IV}+0.250E_{II}+0.125E_{I}. \quad (25)$$

The lowest average electron energy of the bands of Fig. 4 for the region between 2 and 3 units of length is found to be -0.55 for $r=2.35$; the observed half-distance between nearest neighbors is $r=2.22$ atomic units. In Fig. 5, obtained from Kimball's solutions, the point of lowest average electron energy as given by (25) is about -0.85 Rydberg unit, occurring almost exactly at the observed half-internuclear distance of 2.22 atomic units.

If we trust the general character of our results apart from the quantitative side, we can say that the absorption band consists of several overlapping bands. There is first the possibility of an absorption starting in the doubly degenerate level IV; since level IV contains all values of $\mathbf{k}$, transitions can occur from IV to any level in the range III to VI. Since the electron level density is usually highest near the middle of an allowed band, and since VI is doubly degenerate, the absorption band starting in IV should have the following character: The long wave limit is due to a transition from IV to III; then, to shorter wave-lengths, follow transitions from IV to the interior of the band between III and V, with first increasing, then decreasing intensities, until V is reached; the end state moves then into the band between V and VI, with a maximum intensity for an end state near the middle between V and VI, whereupon the intensity decreases again. At the short wave-length limit, there is almost a strong line, due to transitions between the degenerate levels IV and VI. This band, therefore, should have its long wave limit for transitions between IV and III, an intense short wave limit due to transitions between IV and VI, and two maxima in between.

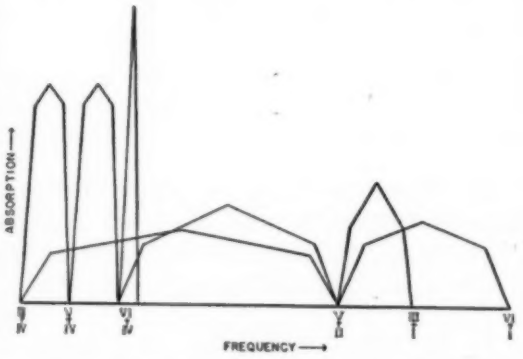

FIG. 6. Schematic plot of absorption bands of silicon based on electronic structure as shown in Fig. 4.

Four other bands in the same region, probably of much smaller absorption coefficient because of the spread of the filled levels, are brought about by electrons coming from the two bands between I and IV and going to the region between III and VI.

There should be one band with a long wave limit due to transitions between IV and III, which coincides with the long wave limit of the band described before, and a short wave limit due to transitions between II and V; immediately adjacent is a band with a long wave limit due to transitions between II and V and a short wave limit due to transitions between I and VI. This extends much farther toward the ultraviolet than does the band originating in the degenerate level IV.

In addition to these, there should be a band with a short wave limit due to transitions between II and V and with a long wave limit due to transitions between IV and VI. Finally, there should be a band where the long wave limit is due to a transition between II and V and the short wave limit to a transition between I and III.

A schematic drawing of the absorption as brought about by these transitions is presented in Fig. 6. It is, of course, impossible to give

[19] W. Shockley, Phys. Rev. **52**, 866 (1937).

[20] This expression is the weighted average of the energies of the occupied bands and is obtained by taking one-fourth the sum of: the energy of the two degenerate bands following curve IV, $2E_{IV}$; the average energy of the band between curves II and IV, approximately $\frac{1}{2}(E_{IV}+E_{II})$; and the average energy of the band between curves II and I, approximately $\frac{1}{2}(E_{II}+E_{I})$.

TABLE V. Values of Z_p and of unnormalized wave functions P at various energies.

Wave function		3s	3s	3s	3s	3s	3s	3p	3p	3p	3p	3d	3d	3d	3d	4f	4f	4f
Negative energy (Rydberg units)		0.0	0.2	0.3	0.6	0.9	1.2	0.0	0.2	0.3	0.6	0.0	0.2	0.3	0.6	0.0	0.3	0.6
r	Z_p																	
0.0	14.00	0.00	0.					0.00				0.00				0.00		
0.01	13.52	0.87						0.01				0.00				0.00		
0.02	13.06	1.50						0.03				0.00				0.00		
0.03	12.62	1.94						0.07				0.00				0.00		
0.04	12.21	2.21						0.12				0.00				0.00		
0.05	11.83	2.35						0.18				0.00				0.00		
0.06	11.48	2.37						0.24				0.00				0.00		
0.07	11.15	2.31						0.31				0.00				0.00		
0.08	10.84	2.17						0.38				0.00				0.00		
0.09	10.56	1.98						0.45				0.01				0.00		
0.10	10.29	1.73						0.52				0.01				0.00		
0.12	9.79	1.15						0.66				0.01				0.00		
0.14	9.34	0.49						0.79				0.02				0.00		
0.16	8.92	−0.20						0.92				0.02				0.00		
0.18	8.52	−0.88						1.03				0.03				0.00		
0.20	8.15	−1.52						1.13				0.04				0.00		
0.24	7.46	−2.66	−2.66	−2.66	−2.66	−2.66	−2.67	1.29				0.06				0.00		
0.28	6.83	−3.53	−3.54	−3.54	−3.54	−3.54	−3.55	1.39				0.08				0.00		
0.32	6.26	−4.14	−4.14	−4.14	−4.15	−4.16	−4.17	1.44	1.44	1.44	1.45	0.11				0.01		
0.36	5.76	−4.48	−4.49	−4.49	−4.50	−4.51	−4.53	1.44	1.44	1.45	1.45	0.14				0.01		
0.40	5.32	−4.60	−4.61	−4.61	−4.63	−4.65	−4.67	1.41	1.41	1.42	1.43	0.17				0.01		
0.44	4.94	−4.52	−4.53	−4.54	−4.57	−4.59	−4.62	1.34	1.35	1.35	1.37	0.21				0.01		
0.48	4.60	−4.27	−4.30	−4.31	−4.34	−4.38	−4.42	1.25	1.26	1.26	1.28	0.24				0.02		
0.52	4.31	−3.90	−3.93	−3.94	−3.99	−4.04	−4.08	1.14	1.15	1.15	1.18	0.29				0.02		
0.56	4.05	−3.42	−3.46	−3.47	−3.53	−3.59	−3.65	1.01	1.02	1.03	1.06	0.33				0.03		
0.60	3.83	−2.86	−2.90	−2.93	−3.00	−3.07	−3.14	0.86	0.88	0.89	0.92	0.38				0.04		
0.68	3.47	−1.59	−1.64	−1.68	−1.77	−1.87	−1.95	0.55	0.57	0.59	0.63	0.48	0.48	0.48	0.49	0.06	0.06	0.06
0.76	3.19	−0.21	−0.27	−0.32	−0.43	−0.55	−0.66	0.21	0.24	0.26	0.31	0.59	0.59	0.60	0.61	0.08	0.08	0.09
0.84	2.97	1.19	1.11	1.05	0.94	0.80	0.67	−0.13	−0.09	−0.08	−0.01	0.70	0.71	0.72	0.73	0.12	0.12	0.12
0.92	2.79	2.53	2.45	2.38	2.26	2.11	1.98	−0.47	−0.43	−0.41	−0.34	0.83	0.84	0.85	0.87	0.16	0.16	0.16
1.00	2.63	3.78	3.70	3.62	3.51	3.36	3.23	−0.80	−0.75	−0.73	−0.66	0.95	0.97	0.98	1.01	0.20	0.21	0.21
1.08	2.49	4.90	4.83	4.75	4.66	4.51	4.39		−1.64		−0.96					0.26	0.27	0.27
1.16	2.36	5.88	5.82	5.75	5.68	5.56	5.46	−1.40	−1.36	−1.33	−1.26	1.22	1.26	1.27	1.33	0.33	0.33	0.34
1.32	2.13	7.36	7.37	7.33	7.36	7.32	7.30	−1.91	−1.88	−1.86	−1.79	1.50	1.56	1.59	1.68	0.49	0.51	0.52
1.48	1.93	8.24	8.36	8.36	8.54	8.64	8.77	−2.32	−2.31	−2.30	−2.26	1.79	1.88	1.92	2.06	0.69	0.73	0.76
1.64	1.75	8.57	8.83	8.90	9.28	9.59	9.92	−2.63	−2.65	−2.66	−2.67	2.09	2.21	2.28	2.48	0.95	1.01	1.06
1.80	1.60	8.44	8.86	9.02	9.66	10.23	10.83	−2.85	−2.91	−2.95	−3.02	2.39	2.57	2.66	2.95	1.27	1.36	1.44
1.96	1.46	7.92	8.54	8.80	9.75	10.64	11.58	−2.98	−3.11	−3.17	−3.33	2.69	2.94	3.06		1.65	1.79	1.92
2.12	1.34	7.09	7.93	8.31	9.62	10.89	12.25	−3.04	−3.24	−3.34	−3.61	3.00	3.33	3.49	4.04	2.09	2.30	2.51
2.28	1.24	6.04	7.11	7.62	9.32	11.04	12.89	−3.04	−3.31	−3.46	−3.86	3.32	3.74	3.96		2.62	2.92	3.22
2.44	1.17	4.81	6.12	6.76	8.90	11.14	13.57	−2.98	−3.35	−3.54	−4.11	3.64	4.18	4.46	5.42	3.22	3.65	4.09
2.60	1.10	3.47	5.01	5.80	8.40	11.22	14.34	−2.87	−3.35		−4.35	3.97	4.65	5.01		3.91	4.50	5.13
2.76	1.05	2.05	3.82	4.75	7.84	11.31	15.23	−2.73	−3.32	−3.64	−4.60	4.30	5.14	5.60	7.15	4.70	5.50	6.37
2.92	1.02	0.59	2.58	3.64		11.45	16.30	−2.55	−3.26		−4.87	4.63	5.67	6.23		5.58	6.12	7.84
3.08	1.00	−0.88	1.30	2.50	6.65	11.64		−2.33	−3.18	−3.65	−5.14	4.96	6.22	6.91	9.35	6.56	7.98	9.58
3.24	1.00	−2.33	0.00	1.33		11.91		−2.10	−3.09		−5.44	5.29	6.80	7.65			9.50	11.61
3.40	1.00	−3.75	−1.29	0.15	5.41	12.26		−1.84	−2.97	−3.61	−5.77	5.62	7.41	8.43	12.13		11.21	13.98
3.56	1.00	−5.11	−2.57	−1.03		12.71		−1.56	−2.84		−6.12	5.93	8.05	9.26			13.14	16.73
3.72	1.00	−6.40	−3.83		4.18	13.27		−1.26	−2.69	−3.53	−6.50	6.23	8.70	10.14	15.58			
4.04	1.00	−8.70	−6.24		2.97	14.77		−0.63	−2.36	−3.42	−7.37	6.78	10.08	12.06	19.82			
4.36	1.00		−8.46		1.80	16.89		0.02	−1.99	−3.28	−8.41		11.53	14.19	25.03			
4.68	1.00		−10.46		0.65	19.78		0.67	−1.58	−3.12	−9.67		13.06	16.55	31.41			
5.00	1.00		−12.21		−0.49	23.63		1.30	−1.15	−2.95	−11.19		14.64	19.16	39.22			

estimates of the relative strengths of these bands without extensive calculations.[18]

The experimental data (Fig. 1) seem to show that the absorption band is complex, but there is no sign of an absorption line due to transitions between degenerate states IV and VI and no sign of the long ultraviolet "wing" that should come from transitions originating in the band between I and II and ending in the band between V and VI.

The writer wishes to acknowledge his indebtedness to Professor K. F. Herzfeld who suggested the problem and the method of solution and who gave much valuable aid in the work. He also wishes to thank Dr. G. E. Kimball of Columbia University and Assistant Professors C. A. Beck and F. E. Fox of Catholic University for suggestions and discussion.

APPENDIX

The field used in the numerical integration of the Schrödinger equation is a self-consistent field in which no account is taken of the correlations giving rise to exchange energy. Since a modification of Hartree's method of obtaining solutions of the Schrödinger equation for the free atom was used in calculating the solutions for the solid,[21]

[21] An account of this method together with a discussion of the error introduced by neglect of exchange may be found in Chapter IX, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

the field of the core functions (with small changes) obtained by McDougall[22] through the simple Hartree self-consistent field method was used in preference to the field calculated more recently,[23] in which exchange terms were considered. The core functions were estimated for neutral silicon by comparing the core functions obtained by McDougall for Si V with those obtained by Donley[24] for Si IV and Si III and then applying small corrections. The extrapolated values differed only slightly from the original values; the error introduced by extrapolation is believed to be far less than that brought in by other approximations. To this core field was added three-quarters the field of a combination of three $3p$ electrons and one $3s$ electron normalized to 3.18 atomic units, the radius of the sphere having the same volume as the cellular polyhedron of silicon. In consideration of the symmetry of the silicon lattice, the use of this spherically symmetrical valence electron field (three-quarters the field of three $3p$ electrons and one $3s$ electron) was thought to be preferable to use of a non-symmetrical field of three valence electrons (the field of two $3s$ electrons and one $3p$ electron, or of one $3s$ and two $3p$ electrons), as would be used in Hartree's procedure for obtaining wave functions for the free atom. Successive approximations were made with energy values for the $3s$ and $3p$ electrons approximately equal to those of the free atom until the expected difference between initial and final fields was not greater than about 0.01 at any point. It was considered needless to seek greater accuracy in the field than this since the other approximations required in building up the wave function of the solid introduce unavoidable error far greater than that brought in by a field of this accuracy.

In Table V is presented, for various values of r, a tabulation of Z_p, the effective nuclear charge for potential, i.e., the point charge which would give, if it were placed at the nucleus, the same potential at radius r as that of the actual field. Also presented in Table V are the unnormalized functions P for various energies; $P=r$ times the radial part of the solution of the Schrödinger equation.

[22] J. McDougall, Proc. Roy. Soc. **A138**, 550 (1932).

[23] W. Hartree, D. R. Hartree, and M. F. Manning, Phys. Rev. **60**, 857 (1941). It is noted here that the optical term values calculated for Si IV and Si V from the field with exchange do not agree as well with experiment as those obtained by McDougall (reference 22) using the wave functions found by methods neglecting exchange in the wave functions but including exchange terms in the expression for energy. The authors conclude that neglect of exchange has two counteracting effects which may balance each other.

[24] H. L. Donley, Phys. Rev. **50**, 1012 (1936).

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On Milne's Theory of Gravitation

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The present paper is a criticism of Milne's theory of the gravitational two-body problem. In particular, it is shown that Milne's theory is not invariant under a Lorentz transformation and therefore, since it is based on "kinematical relativity," is inconsistent.

1

IN a series of papers,[1] Milne claims to have obtained an "expression of the inverse square law, or its potential $1/r$, in a form relativistically invariant under Lorentz-transformation from any one fundamental observer to any equivalent observer."[2] The purpose of this paper is to show that Milne's theory of gravitation, contrary to this and other similar assertions, is not invariant under a Lorentz-transformation.

Milne, in his writing, deliberately foregoes "any mention of the construct 'space-time.'"[3] However, the four-dimensional tensor-notation not only enables us to rewrite formulae in a form more compact than is possible in the inappropriate three-dimensional vector calculus; it also contributes to greater clarity. The covariance of a relation under Lorentz transformations is easily tested if the four-dimensional tensor calculus is used consistently.

We denote the coordinates of an event by x^i $(i=0, 1, 2, 3)$ or alternatively, when the occasion arises, by (t, x, y, z). The usual summation-convention applies to double indices. Since we are concerned only with special relativity, our metric form is that of Minkowski space:

$$ds^2=\eta_{ij}dx^i dx^j, \quad \eta_{ij}=\eta_{ji} \\ =dt^2-dx^2-dy^2-dz^2. \tag{1}$$

(The velocity of light c is taken equal to 1.)

In order to avoid confusion, it is well to distinguish clearly between a particle and an event. Much of the criticism in this paper is caused by Milne's failure to differentiate sufficiently between these concepts. For our purpose, we may define a particle simply as a world line,[4] i.e., a curve $x^i=x^i(\theta)$ in space-time, θ being some arbitrary parameter along the curve (usually the "propertime" s or the coordinate t). With a particle or world line may be associated physical scalars such as the rest mass m, the electric charge e, etc. An event, of course, is a point completely determined by its four coordinates x^i.

2

The fundamental problem which Newton's theory of gravitation solves in principle is the following: Given initial positions and velocities of an isolated system of gravitating particles, i.e., given the points of intersection of their world lines with the plane $t=$const. and the directions of the world lines at these points, to find the world lines. Newton's theory enables us to write down a second-order differential equation for each world line; the unique solution of the system of equations with the given initial conditions can then be shown to exist.

As is well known, the classical theory of gravitation, like all theories involving action-at-a-distance force laws, is not "Lorentzinvariant." This is understood to mean that the differential equation of the world line of a particle is changed in form under Lorentz transformations; alternatively, if observers in different Lorentz frames use such a theory to calculate the world line of a particle, they will in general obtain different curves. This deficiency of the Newtonian law of attraction is immediately traced to the fact that in the theory of relativity simultaneity of distant events is not an absolute concept, but is meaningful only in a fixed inertial frame. Precisely the

[1] E. A. Milne, I, II, III, Proc. Roy. Soc. **A156**, 62–85 (1936); **160**, 1–23, 24–36 (1937); and IV, Phil. Mag. [VII] **34**, 82–101 (1943); hereafter referred to as I, II, III, IV, respectively.
[2] IV, Sec. 35, p. 96.
[3] IV, Sec. 13, p. 84.
[4] In order to adhere to common usage, the expression "world line of a particle" will be utilized in the following, although our definition permits us to replace it by the one word "particle."

same argument also applies to Milne's formulation of the inverse square law.

3

First, however, mention will be made of a minor difficulty in Milne's analysis. The coordinates x^i of an event are in general not components of a vector; only the coordinate-distance between two events x^i and $x_{(0)}{}^i$, i.e., $x^i - x_{(0)}{}^i$, is a vector. Milne considers only Lorentz frames (his "fundamental observers") with a common origin O, chosen at the point in space-time where his model of the expanding universe is initially concentrated, i.e., the common point of intersection of all world lines. Thus, limiting himself to Lorentz transformations which correspond to rotations only of the coordinate frame, he can consistently put $x_{(0)}{}^i \equiv 0 \equiv (o, o, o, o)$ and hence treat x^i as a contravariant vector. In the following we shall retain this particular aspect of Milne's cosmological model and limit ourselves to Lorentz frames with the common "natural origin." But it is well to emphasize that this aspect of Milne's cosmology (which is common also to some other cosmological theories) is a prerequisite to his formulation of the inverse square law;[5] if the former is repudiated, the latter loses all significance.

4

A system of two particles under mutual gravitational attraction is considered, the rest masses being $m_{(1)}$ and $m_{(2)}$. Let us assume that the world lines of these particles have been obtained and investigate whether Milne's differential equations of motion can be satisfied by the world lines irrespective of the Lorentz frame.

Let $P_{(1)} \equiv x_{(1)}{}^i$, $P_{(2)} \equiv x_{(2)}{}^i$ be events on the two world lines. We construct a "potential" χ:

$$\chi = -\frac{m_{(1)}m_{(2)}}{M_0} \cdot \frac{x_{(1)j}x_{(2)}{}^j}{\{(x_{(1)k}x_{(2)}{}^k)^2 - x_{(2)k}x_{(2)}{}^k \cdot x_{(1)r}x_{(1)}{}^r\}^{\frac{1}{2}}}, \quad (2)$$

where M_0 is a constant which plays the role of the constant of gravitation and $x_j = \eta_{jk}x^k$, as is suggested by the notation. Milne's equations of motion,[6] written in tensor notation, are

$$\frac{d}{ds_{(1)}}\left(m_{(1)}\xi_{(1)}{}^{\frac{1}{2}}\frac{dx_{(1)}{}^i}{ds_{(1)}}\right) + \frac{m_{(1)}\xi_{(1)}{}^{\frac{1}{2}}}{x_{(1)k}x_{(1)}{}^k}\left(x_{(1)}{}^i - x_{(1)r}\cdot\frac{dx_{(1)}{}^r}{ds_{(1)}}\cdot\frac{dx_{(1)}{}^i}{ds_{(1)}}\right) - 2\frac{dx_{(1)}{}^i}{ds_{(1)}}\cdot\frac{d}{ds_{(1)}}(m_{(1)}\xi_{(1)}{}^{\frac{1}{2}}) = \eta^{ij}\frac{\partial\chi}{\partial x_{(1)}{}^j} \quad (3)$$

$$\frac{d}{ds_{(2)}}\left(m_{(2)}\xi_{(2)}{}^{\frac{1}{2}}\frac{dx_{(2)}{}^i}{ds_{(2)}}\right) + \frac{m_{(2)}\xi_{(2)}{}^{\frac{1}{2}}}{x_{(2)k}x_{(2)}{}^k}\left(x_{(2)}{}^i - x_{(2)r}\cdot\frac{dx_{(2)}{}^r}{ds_{(2)}}\cdot\frac{dx_{(2)}{}^i}{ds_{(2)}}\right) - 2\frac{dx_{(2)}{}^i}{ds_{(2)}}\cdot\frac{d}{ds_{(2)}}(m_{(2)}\xi_{(2)}{}^{\frac{1}{2}}) = \eta^{ij}\frac{\partial\chi}{\partial x_{(2)}{}^j} \quad (4)$$

where[7]

$$\xi_{(1)} = \frac{\left(x_{(1)j}\frac{dx_{(1)}{}^j}{ds_{(1)}}\right)^2}{x_{(1)k}x_{(1)}{}^k} \quad \text{and} \quad \xi_{(2)} = \frac{\left(x_{(2)j}\frac{dx_{(2)}{}^j}{ds_{(2)}}\right)^2}{x_{(2)k}x_{(2)}{}^k}.$$

If Eqs. (3) and (4) together with initial conditions (see Section 2) are to yield solutions $x_{(1)}{}^i = x_{(1)}{}^i(s_{(1)})$, $x_{(2)}{}^i = x_{(2)}{}^i(s_{(2)})$, a relationship between the two parameters $s_{(1)}$ and $s_{(2)}$ must be postulated, to be applied to the partial derivatives of χ in the equations of motion. To put it differently, given a value of $s_{(1)}$, i.e., given an event $P_{(1)}$ on the first world line, the differential equation (3) tells us about the behavior of the world line at $P_{(1)}$ only if we know how to determine $\partial\chi/\partial x_{(1)}{}^i$ which depends not only on $P_{(1)}(s_{(1)})$ but also on an event $P_{(2)}(s_{(2)})$ on the second world line. We must have a rule for associating an event $P_{(1)}(s_{(1)})$ with an event $P_{(2)}(s_{(2)})$, i.e., a relation between $s_{(1)}$ and $s_{(2)}$. A corresponding argument applies to Eq. (4). It should be mentioned, however, that the relations between $s_{(1)}$ and $s_{(2)}$ need not in general be symmetric and that we obtain the relation which is to be applied to Eq. (4) by interchanging suffixes "(1)" and "(2)" in that applied to Eq. (3).

Equations (3) and (4) are apparently in tensor form, but they are in general true tensorial equations if and only if χ behaves like a scalar under Lorentz transformations. This is the case

[5] Also to Milne's theory of rational electrodynamics, Proc. Roy. Soc. **A165**, 313–332, 333–357 (1938); and Phil. Mag. [VII] **34**, 73–101, 197–211, 235–258 (1943).

[6] II, Sec. 11, p. 12, Eqs. (45), (45′), (46), (46′).

[7] $ds_{(1)}$ and $ds_{(2)}$ are given by (1), i.e., $ds_{(1)}{}^2 = \eta_{ij}dx_{(1)}{}^i dx_{(1)}{}^j$; $ds_{(2)}{}^2 = \eta_{ij}dx_{(2)}{}^i dx_{(2)}{}^j$.

if in Eq. (3) [or (4)] an event $x_{(2)}{}^i$ (or $x_{(1)}{}^i$) is associated with each event $x_{(1)}{}^i$ (or $x_{(2)}{}^i$) in a manner independent of the frame of reference. Otherwise Milne's equations are not invariant under Lorentz transformations. Milne uses simultaneity[8]—$t_{(1)}=t_{(2)}$—to set up a symmetric correspondence between events on the two world lines. This correspondence does, of course, depend on the particular frame of reference. If one observer finds that the two world lines satisfy Eqs. (3) and (4) with $t_{(1)}=t_{(2)}$, a second observer may fail to do so. Thus the theory is not invariant under a Lorentz transformation.

Repeating, we may say that Eqs. (3) and (4) alone are invariant but meaningless as equations of motion. By adding the relation of simultaneity, the equations of motion become meaningful but lose their Lorentz invariance. Milne anticipates this in part when he says, "Of course the interpretative relation $t_{(1)}=t_{(2)}=t$ is not invariant,"[9] but he fails to draw the conclusion that the invariant character of his whole gravitational theory is affected.

It is not difficult to construct a correspondence which is invariant. As an example[10] we consider the light cone with $x_{(1)}{}^i \equiv P_{(1)}$ as vertex and with its axis pointing to the past. Its equation in any Lorentz frame is $(x^i-x_{(1)}{}^i)(x_i-x_{(1)i})=0$. We now define $P_{(2)}$ corresponding to $P_{(1)}$ as the point of intersection of the cone and the second world line. Interchanging suffixes "(1)" and "(2)," we obtain the relation to be applied to $\partial\chi/\partial x_{(2)}{}^i$ in Eq. (4). This is the well-known method of the retarded potential. However, the advanced potential or any linear combination of the two could be used equally well. Thus, to make the theory relativistically invariant, new and to some extent arbitrary assumptions have to be added which destroy the epistomological character of Milne's theory.

5

There is an exceptional case in which one of the two equations of motion is invariant under Lorentz transformations. If the world line of the attracting particle, say the second, is a straight line through the common origin O, i.e., if its equation is $x_{(2)}{}^i=\lambda^i s_{(2)}$,[11] where λ^i is an arbitrary unit vector, then

$$\chi=-\frac{m_{(1)}m_{(2)}}{M_0}\cdot\frac{\chi_{(1)j}\lambda^j}{\{(x_{(1)k}\lambda^k)^2-x_{(1)k}x_{(1)}{}^k\}^{\frac{1}{2}}},\quad \lambda^i\lambda_i=1, \tag{5}$$

and χ is independent of $s_{(2)}$ and hence of $x_{(2)}{}^i$. We then have a one-body problem with the equation of motion (3), and the arguments of the previous paragraph do not apply. In fact, we have the case of one particle moving in a given external field of force. In all applications of his theory, this is the case which Milne assumes, although no explicit mention is made of it. A coordinate system is chosen in which the attracting particle is at rest, i.e., such that its world line coincides with the t axis; this of course implies that the world line is a straight line through the origin.[12]

In Section 15 of II, Milne generalizes his theory to a system of n particles. Again, the theory is relativistically invariant only if the world lines of $n-1$ particles are straight lines through the origin, and then only the equation of motion of the last particle is given.

That Milne does not himself wish to limit his theory to the one-body problem discussed in this section can be gathered from the following quotation:

"The core of the present paper is . . . to obtain a general formula for the potential energy χ of *any* two massive particles $m_{(1)}$ and $m_{(2)}$. . . . It is applied to obtain the *relativistic* equations of motion . . . of *any* two particles in one another's presence."[13]

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[8] II, Sec. 11, p. 13.

[9] II, Sec. 9, (1), p. 7.

[10] Compare Milne, Proc. Roy. Soc. **A165**, Sec. 12, 340 (1938).

[11] It should be noticed that Eqs. (3) and (4), which are Milne's Eqs. (45), (45′), (46), (46′) of II, Sec. 11, p. 12 are not both satisfied by $x_{(2)}{}^i=\lambda^i s_{(2)}(m_{(1)}, m_{(2)}, \text{finite})$; since in this case $\xi_{(2)}=1$, $\frac{dx_{(2)}{}^i}{ds_{(2)}}=\lambda^i$, and Eq. (4) (on multiplication by η_{ij}) yields

$$\frac{\partial\chi}{\partial x_{(2)}{}^j}=0=\frac{m_{(1)}m_{(2)}}{M_0}\cdot\frac{x_{(1)k}x_{(1)}{}^k}{\{(x_{(1)i}x_{(2)}{}^i)^2-x_{(1)i}x_{(1)}{}^i\cdot x_{(2)k}x_{(2)}{}^k\}^{\frac{1}{2}}}\cdot(x_{(1)i}x_{(2)}{}^i x_{(2)j}-x_{(2)i}x_{(2)}{}^i x_{(1)j})$$

$$=\frac{m_{(1)}m_{(2)}}{M_0}\cdot\frac{x_{(1)k}x_{(1)}{}^k}{\{(x_{(1)i}\lambda^i)^2-x_{(1)i}x_{(1)}{}^i\}^{\frac{1}{2}}}\cdot\frac{1}{s_{(2)}}\cdot(x_{(1)i}\lambda^i\lambda_j-x_{(1)j}).$$

Hence $x_{(1)i}\lambda^i\lambda_j=x_{(1)j}$, $x_{(1)j}$ is parallel to λ_j, and thus finally $x_{(1)j}=\lambda_j s_{(1)}$. This shows that the two particles coincide, χ becomes infinite and the problem of gravitation loses all significance.

[12] II, Sec. 17, p. 15; and IV, Secs. 33, 34, p. 95; the argument of Sec. 34 only holds in the case we are considering.

[13] II, Sec. 2, p. 2; italics are my own.

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A Calculus of Finite Precision

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Sec. I. This paper inverts certain quantum mechanical ideas by constructing a "probability of presence" from first principles. If $x_i=f_i(s, a_1, a_2)$ represents a 2-parameter family of curves in 3-dimensional space, the density of the functions f_i with respect to the parameters a_1a_2 is defined by means of an expression for the normal cross section of a sheaf of curves. This density plays the role of a probability. Its derivative along a curve of the family is independent of the parameters a_1a_2. This circumstance permits a special density to be constructed, called the "characteristic" or "smoothest" density, which is independent of the parameters and which can be found by solving a linear second-order partial differential equation. The extension to n-dimensional space and $(n-1)$ parameters is given. *Sec. II.* The concept of orbital density is the dynamical equivalent of the density of Sec. I. Dividing the orbital density by the velocity of the representative point gives the quantity we call kinematical probability P, which satisfies the fundamental equation (2.8), and which has the same force as any other probability of presence. Equation (2.8) is used to derive from the Hamilton-Jacobi equation a "wave" equation for $\sqrt{P}$ for a system of n planets moving around a sun under the condition that the space average of the mutual interactions of the planets is a minimum. This provides a new approach to planetary dynamics and yields an equation that is very much like Schroedinger's equation for the stationary states of n particles, and has the same basic interpretation. *Sec. III.* A non-conservative system of n particles is assumed to be in a state such that the action function can be written $W=-Et+R(x_i, t)$ in which R still contains the time explicitly. Starting with the Hamilton-Jacobi equation, using Eq. (2.8), and imposing the condition that the space average of $\partial R/\partial t$ is a minimum, an equation [*viz.*, (3.10)] is derived which differs from Schroedinger's equation for stationary states only in certain respects that cannot be regarded as fundamental. Despite this basic equivalence of Schroedinger's equation and our equation (3.10), conflicts in interpretation and formalism arise which are briefly discussed. *Sec. IV.* Complex U's are introduced into Eq. (3.10) in a simple way which fails to bridge the gap between our formalism and that of quantum mechanics. The kinematical probability defined by Eq. (3.10) is shown to have the "smoothest" property. To account physically for the stationary states an electromagnetic wave system is proposed which has the property that a particle moving in it may be in "phase-mechanical" resonance with it. Macroscopic examples of this kind of resonance are given. This concept represents an inversion of physical ideas of quantum mechanics corresponding to the mathematical inversion with which we began.

I. INTRODUCTION

THE mathematical theory presented here is an inversion of quantum-mechanical ideas in the sense that instead of determining a probability density or probability "of presence" by solving a prescribed differential equation, we *construct* such a probability *ab initio* from elementary geometric or mechanical concepts and determine some of its properties. The first results evolving from this construct were presented at a recent meeting of the American Physical Society;[1] here they will be generalized and amplified.

Let the solutions of the system of differential equations

$$\frac{dx_1}{X_1}=\frac{dx_2}{X_2}=\frac{dx_3}{X_3} \tag{1.1}$$

be of the form

$$x_i=f_i(s, a_1, a_2). \tag{1.2}$$

Here the X_i, as functions of the x_j, are single-valued or else confined to one branch; if the X_i contain any parameters b_k, they will be supposed *fixed*. Then Eq. (1.2) defines a 2-parameter system of curves in a 3-dimensional space through each point of which passes one and only one curve (except at singular points). The independent variable s in Eq. (1.2) measures distance along any such curve. These equations determine a system of unit tangent vectors $\mathbf{t}$ given by

$$t_i=\frac{dx_i}{ds}=X_i(\sum X_j^2)^{-\frac{1}{2}} \tag{1.3}$$

which may be expressed as functions of the x_k or of s, a_1, a_2.

By means of the displacement

$$\delta\mathbf{s}=\left(\mathbf{i}\frac{\partial x_1}{\partial a_1}+\mathbf{j}\frac{\partial x_2}{\partial a_1}+\mathbf{k}\frac{\partial x_3}{\partial a_1}\right)\delta a_1$$

$$=\frac{\partial \mathbf{s}}{\partial a_1}\delta a_1\left(\text{definition of }\frac{\partial \mathbf{s}}{\partial a_1}\right),$$

[1] B. Liebowitz, Phys. Rev. 65, 255 (1944).

in which a_1 alone is varied, we pass from a given point on a given curve to a nearby point on a neighboring curve. The normal distance between the two curves is

$$\delta\mathbf{n}_1=\left(\frac{\partial\mathbf{s}}{\partial a_1}\times\mathbf{t}\right)\delta a_1,$$

where the components of $\mathbf{t}$ are given by Eq. (1.3). Likewise if a_2 alone is varied, the normal distance to a *different* neighboring curve, assuming a_1 and a_2 are independent, is given by

$$\delta\mathbf{n}_2=\left(\frac{\partial\mathbf{s}}{\partial a_2}\times\mathbf{t}\right)\delta a_2.$$

The vector $\delta\mathbf{n}_1\times\delta\mathbf{n}_2$ is tangential to the curve; its magnitude represents the normal area pierced by the sheaf of curves comprised between $x_i(s, a_1, a_2)$ and $x_i(s, a_1+\delta a_1, a_2+\delta a_2)$. The *density* of the curves is obviously inversely proportional to this area. Hence we *define* the density Q of the functions f_i with respect to the parameters a_1a_2 by the equation

$$\frac{\mathbf{t}}{Q}=\frac{\delta\mathbf{n}_1\times\delta\mathbf{n}_2}{\delta a_1\delta a_2}=\left(\frac{\partial\mathbf{s}}{\partial a_1}\times\mathbf{t}\right)\times\left(\frac{\partial\mathbf{s}}{\partial a_2}\times\mathbf{t}\right) \tag{1.4}$$

$$=\left(\frac{\partial\mathbf{s}}{\partial a_1}\cdot\frac{\partial\mathbf{s}}{\partial a_2}\times\mathbf{t}\right)\mathbf{t}$$

or

$$\frac{1}{Q}=\begin{vmatrix} t_1 & t_2 & t_3 \\ \dfrac{\partial x_1}{\partial a_1} & \dfrac{\partial x_2}{\partial a_1} & \dfrac{\partial x_3}{\partial a_1} \\ \dfrac{\partial x_1}{\partial a_2} & \dfrac{\partial x_2}{\partial a_2} & \dfrac{\partial x_3}{\partial a_2} \end{vmatrix}. \tag{1.5}$$

The determinant is to be taken positive. It depends obviously on the parameters a_1a_2, but the derivative of $\log Q$ in the direction of the curve does not. For it is not difficult to prove that

$$-\frac{1}{Q}\frac{dQ}{ds}=\nabla\cdot\mathbf{t}, \tag{1.6}$$

and since the components of $\mathbf{t}$ can be obtained by Eq. (1.3) directly from the differential equation (1.1), it follows that the derivative of the logarithm of the density Q taken along a curve (1.2) is independent of the choice of the parameters a_1a_2. The derivative in any other direction *is* dependent on the a's.

The density Q has the force of a probability of presence. It will be clear from the definition that if a point 0 is constrained to lie on a curve of the set defined by Eq. (1.2) and if the a's are chosen so that all values of a_1 and a_2 are equally probable, then the probability of finding the point 0 in the volume element $dxdydz$ is proportional to $Qdxdydz$. If it is desired to know the average value of some property of the functions (1.2), e.g., the square of the gradient of the density Q, it is only necessary to form the integral $\int(\nabla Q)^2Qd\tau/\int Qd\tau$ over the domain of interest. In general, the density Q will depend on the choice of a_1 and a_2, but it is possible to define a density Q_e which will be called the "smoothest" density or "characteristic" density, which has special properties and which does not depend on the a's, but does depend on certain boundary conditions, as will be shown.

If the derivative of Q in all directions perpendicular to $\mathbf{t}$ should vanish, then $(1/Q)(dQ/ds)$ would represent the gradient of $\log Q$. Obviously this would be a very special case. More generally, $[(1/Q)(dQ/ds)]^2$ represents the smallest value which the square of the gradient of $\log Q$ can have. Let G^2 represent the difference between the square of the actual gradient of $\log Q$ and the square of this minimum value. Then the characteristic density is defined as that density which, on the average, makes this difference a minimum. In symbols

$$G^2=(\nabla\log Q)^2-\left(\frac{d}{ds}\log Q\right)^2=(\nabla\log Q)^2-(\nabla\cdot\mathbf{t})^2,$$

$$\delta\int G^2Q_ed\tau=0.$$

Putting $Q_e=\varphi^2$, we find the variational equation is

$$\delta\int\left\{\Sigma\left(\frac{\partial}{\partial x_i}\log\varphi\right)^2-\tfrac{1}{4}(\nabla\cdot\mathbf{t})^2\right\}\varphi^2d\tau=0,$$

which leads, by the usual rules, to the necessary condition

$$\Sigma\frac{\partial^2\varphi}{\partial x_i^2}+\left(\frac{\nabla\cdot\mathbf{t}}{2}\right)^2\varphi=0, \tag{1.7}$$

subject to appropriate *boundary conditions*.

This result depends, of course, on the existence of the integral to be minimized, but not on the prenormalization of φ^2 because φ can be multiplied by an arbitrary constant before the variation and/or after without altering anything. The equivalent of Eq. (1.6) is given for two dimensions in reference 1; Eq. (1.7) was presented at the meeting cited but is not printed in the reference.

The generalization to an $(n-1)$-parameter family in n-dimensional space is immediate. For example, the generalization of the definition Eq. (1.5) for the density Q is

$$\frac{1}{Q}=\begin{vmatrix} t_1 & t_2 & \cdots & t_n \\ \dfrac{\partial x_1}{\partial a_1} & \dfrac{\partial x_2}{\partial a_1} & \cdots & \dfrac{\partial x_n}{\partial a_1} \\ \dfrac{\partial x_1}{\partial a_2} & \dfrac{\partial x_2}{\partial a_2} & \cdots & \dfrac{\partial x_n}{\partial a_2} \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{\partial x_1}{\partial a_{n-1}} & \dfrac{\partial x_2}{\partial a_{n-1}} & \cdots & \dfrac{\partial x_n}{\partial a_{n-1}} \end{vmatrix}. \tag{1.8}$$

Equations (1.6) and (1.7) remain formally unchanged and so does the meaning of Q as a probability of presence. The corresponding system of differential equations is now

$$dx_1/X_1=dx_2/X_2=\cdots=dx_n/X_n. \tag{1.9}$$

These concepts, definitions, and equations represent a definite step toward the construction of a "calculus of finite precision," which, it is believed, is of intrinsic interest for both mathematics and physics. We shall not undertake here to illustrate the application of this calculus to purely mathematical matters; in the next section we shall present an application to dynamics.

II. APPLICATION TO DYNAMICS

We consider a dynamical system of n particles moving in a field of force determined by a potential V which may contain the time explicitly. The action function W, which is the solution of the Hamilton-Jacobi equation

$$\frac{\partial W}{\partial t}+\frac{1}{2}\sum_{k=1}^{3n}\frac{1}{m_k}\left(\frac{\partial W}{\partial x_k}\right)^2+V=0, \tag{2.1}$$

will in general contain, beside the $3n$ coordinates x_i, $3n$ parameters c_j, and the time t. We suppose that the parameters c_j are *fixed*, and that the time is frozen at some instant t_0. Then the $3n$-dimensional configuration space will be filled with a frozen system of action surfaces

$$W(x_i, c_j, t_0)=C \tag{2.2}$$

and of orbits normal thereto.

The momenta

$$p_k=\partial W/\partial x_k \tag{2.3}$$

determine a system of unit tangents to the orbits, *viz.*,

$$t_i=\frac{p_i}{p}=p_i(\textstyle\sum p_j^2)^{-\frac{1}{2}}=\dfrac{\partial W}{\partial x_i}\left(\sum\left(\dfrac{\partial W}{\partial x_j}\right)^2\right)^{-\frac{1}{2}}, \tag{2.4}$$

so that the equations of the orbits may be written

$$dx_1/p_1=dx_2/p_2=\cdots=dx_{3n}/p_{3n}. \tag{2.5}$$

The only difference between Eqs. (1.9) and (2.5) lies in the circumstance that the X_i in (1.9) are given functions of the x_j and the parameters b_k (supposed fixed), whereas the p_i of (2.5) are unknown but nevertheless definite functions of the x_j and the parameters c_k (also supposed fixed). The apparatus of the calculus of finite precision described in the first section is therefore applicable; the only change we make is one of nomenclature—we call the density of solutions of Eq. (2.5) the *orbital density*, but retain the same symbol Q. Using the values of t_i given by Eq. (2.4) we have

$$\begin{aligned}\nabla\cdot\mathbf{t}&=\sum\frac{\partial t_i}{\partial x_i}=\sum\frac{\partial}{\partial x_i}\frac{p_i}{p}\\ &=\frac{1}{p}\left(\nabla\cdot\mathbf{p}-\frac{dp}{ds}\right),\end{aligned} \tag{2.6}$$

so that Eq. (1.6) for the orbital density becomes

$$-\frac{d}{ds}\log\frac{Q}{p}=\frac{\nabla\cdot\mathbf{p}}{p}. \tag{2.7}$$

Now the *kinematical probability* P, or the probability of presence of the representative point in the volume element $dx_1\cdots dx_{3n}$, is directly proportional to the orbital density Q and inversely proportional to the velocity $(\sum(\dot{x}_i)^2)^{\frac{1}{2}}$

$=(\sum(p_i/m_i)^2)^{\frac{1}{2}}$. For the present, let it be assumed that all the masses are equal; then $P=$const. $\times Q/p$ and Eq. (2.7) becomes

$$-\frac{d}{ds}\log P=\frac{\nabla\cdot\mathbf{p}}{p}. \tag{2.8}$$

This equation is given in reference 1 for one particle. *It can be derived for n particles by the method there used*, but the present derivation is more general and reveals the dependence of grad P on the choice of parameters like the a_i of Eq. (1.2). The restriction to equal masses is not essential; it can be removed at any time by going over to a space $\xi_i=x_i\sqrt{m_i}$.

Equation (2.8) is the basic theorem of our dynamics. For subsequent applications it is useful to transform it by first using $p=dW/ds$, so that it becomes

$$-\frac{d\log P}{dW}=\frac{\nabla\cdot\mathbf{p}}{p^2},$$

and then transforming W by writing[2]

$$W=\pm k\log U. \tag{2.9}$$

Equation (2.8) thus becomes

$$\frac{d\log P}{d\log U}=\mp k\frac{\nabla\cdot\mathbf{p}}{p^2}. \tag{2.10}$$

Our first application is to the following classical problem: Given n planets moving about a sun, under what condition will the average of the mutual interaction potential of the planets be a minimum? Let the masses be all equal (a non-essential restriction, as mentioned above); using an obvious notation, write V_1 for $-G\sum Mm_j/r_j$ and V_2 for $-G\sum m_im_j/r_{ij}$; then, since the system is conservative, the action function W may be written as $-Et+S(x_i)$ and the H.J. equation becomes

$$\frac{1}{2m}\sum_{k=1}^{3n}\left(\frac{\partial S}{\partial x_k}\right)^2-(E-V_1)=-V_2.$$

Now introduce $S=\pm K\log U$, multiply by U^2, and integrate over the $3n$-dimensional space; the result is

$$\int\left\{\sum\left(\frac{\partial U}{\partial x_k}\right)^2-\frac{2m}{K^2}(E-V_1)U^2\right\}d\tau=-\frac{2m}{K^2}\int V_2U^2d\tau.$$

If U^2 were identified with the kinematical probability P, the right side of this equation would be equal to the average value of the mutual interaction potential of the planets, and equating its variation to zero would furnish the answer sought. Assume this to be the case; then, subject to appropriate boundary conditions, the variational equation leads, by the usual rules, to the necessary condition

$$\sum\frac{\partial^2U}{\partial x_k^2}+\frac{p_1^2}{K^2}U=0, \tag{2.11}$$

where $p_1^2=2m(E-V_1)$. Using $U=\exp(\pm S/K)$ and $p_i=\partial S/\partial x_i$, we find this condition becomes

$$\nabla\cdot\mathbf{p}=\mp\frac{p^2+p_1^2}{K}. \tag{2.12}$$

But if, as in the case of the solar system, the total momentum of the mutual perturbations of the planets is relatively very small, p^2 and p_1^2 are nearly equal, and Eq. (2.12) becomes $\nabla\cdot\mathbf{p}=\mp 2p^2/K$. When this is inserted in Eq. (2.10) (with K for k), the result is $P=$const.$\times U^2$. Thus the assumption about U is verified to the extent that the momentum owing to mutual perturbations of the planets is small compared with the total momentum of the system.

Equation (2.8) and its equivalent (2.10) are, I believe, entirely rigorous. The only lack of rigor in our derivation of Eq. (2.11) lies in the sufficiency hiatus, but it is unlikely that physicists will cavil about that. (The momentum approximation does not constitute a *logical* weakness.) There are two noteworthy features of these results: (1) a new approach has been found to the basic classical problem of planetary motion (cf. Bode's law), and (2) an equation which is the same in *form and meaning* as Schroedinger's has been derived by substantially rigorous means, *purely classically* for a *purely classical problem*. The constant K can be determined, as soon as U

[2] Compare Schroedinger *Abhandlungen zur Wellenmechanik* (J. A. Barth, Leipzig, 1928), p. 1.

and a single component of momentum are known, from $p_j = \pm (K/U)(\partial U/\partial x_j)$, subject, however, to certain characteristics of momenta whose divergence is zero, as will be brought out in the next section.

III. APPLICATION TO ATOMIC DYNAMICS

It is surprising how quickly the construct we have called kinematical probability leads to formalisms like those of quantum mechanics. Starting with the basic theorem (Eq. 2.8)

$$-\frac{d}{ds}\log P = \frac{\nabla\cdot\mathbf{p}}{p}, \tag{3.1}$$

and transforming it by means of Eq. (2.9),

$$W = \pm k \log U, \tag{3.2}$$

the result as found in Section II (Eq. 2.10) is

$$\frac{d\log P}{d\log U} = \mp\frac{\nabla\cdot\mathbf{p}}{p^2}k. \tag{3.3}$$

Now if *either* of the two following equations is assumed,

$$P = \text{const.} \times U^2, \tag{3.4}$$

$$\nabla\cdot\mathbf{p} = \mp\frac{2p^2}{k}, \tag{3.5}$$

the *other* follows. Also if Eq. (3.5) is entered with $p_i = \partial W/\partial x_i = \pm(k/U)(\partial U/\partial x_i)$, it becomes

$$\Sigma\frac{\partial^2 U}{\partial x_i^2} + \frac{p^2}{k^2}U = 0. \tag{3.6}$$

Furthermore, the formula for the average of a momentum component becomes

$$\bar{p}_j = \int p_j U^2 d\tau = \pm k\int U\frac{\partial U}{\partial x_j}d\tau;$$

likewise corresponding formulae for $\bar{p}_j^2$, etc. are obtained, provided that after partial integration, the integrated part $U\partial U/\partial x_j$ can be assumed to vanish.

Equation (3.6) is just the same in form and meaning as Schroedinger's and the formulae for the momentum averages are very similar to those of quantum theory. There are differences, to be sure, which will be discussed below. And there is conflict! Thus, where we write $p_i = \pm(k/U)(\partial U/\partial x_i)$, quantum formalism writes $p_j U = (h/i)(\partial U/\partial x_j)$ which has *only operational* significance and in which $\sqrt{-1}$ enters in place of our ± 1. Before discussing this conflicting parallellism we shall show that Eq. (3.6) can be derived straight from the H. J. equation by means of our basic theorem without assuming either (3.4) or (3.5).

Except in the planetary problem, all our equations are applicable to non-conservative systems, i.e., systems in which the potential energy contains the time explicitly. Let us assume, however, that the system under consideration, though non-conservative, is nevertheless in a "stationary state," by which we mean that the system is in a quasi-conservative state such that it hovers around a definite energy E. Corresponding to this we may write

$$W = -Et + R(x_i, t), \tag{3.7}$$

which differs from the usual form in that R still contains the time. The H. J. equation now reads (with all masses equal)

$$\frac{1}{2m}\Sigma\left(\frac{\partial R}{\partial x_i}\right)^2 - (E-V) = -\frac{\partial R}{\partial t}.$$

Now use Eq. (3.2) (with R for W), multiply through by U^2, and integrate over the $3n$-dimensional volume; the result is

$$\int\left\{\frac{k^2}{2m}\Sigma\left(\frac{\partial U}{\partial x_i}\right)^2 - (E-V)U^2\right\}d\tau = -\int\frac{\partial R}{\partial t}U^2 d\tau. \tag{3.8}$$

For a conservative system, the right side of Eq. (3.8) vanishes identically. Our non-conservative system will be in a state nearest to conservative if the space average of $\partial R/\partial t$ is a minimum. We therefore impose the condition

$$-\delta\int\frac{\partial R}{\partial t}P d\tau = 0. \tag{3.9}$$

Once more we tentatively identify P with U^2. The resulting variational problem leads, by the usual rules, to the necessary condition

$$\Sigma\frac{\partial^2 U}{\partial x_i^2} + \frac{2m}{k^2}(E-V)U = 0, \tag{3.10}$$

subject, of course, to appropriate boundary conditions. Enter this with $U=\exp(\pm R/k)$ and $p_i=\partial R/\partial x_i$; it becomes

$$\nabla\cdot\mathbf{p}=\mp 2p^2/k. \tag{3.5}$$

If we use this in Eq. (3.3) we verify the identification of P with U^2 and complete the derivation of the Schroedinger equation (3.10) classically. Furthermore, it has been demonstrated that Eq. (3.5) is an alternative way of writing Eq. (3.10).

Although Eq. (3.10) has exactly the same form as Schroedinger's equation for stationary states, and although the dependent variable in both instances is a "probability amplitude," nevertheless there are differences with respect to k, U, and V which must be discussed. Concerning k, Schroedinger identified his constant with Planck's on phenomenological grounds; we do the same, although we hope ultimately to find a logical basis for writing $k=h$. (Cf. the determination of K in the astronomical problem in Section II.) The first difference then is nil.

The second difference concerns the admission of complex U's into Eq. (3.10). This will be taken up in Section IV below, but here we wish to point out that so far as stationary states are concerned, the admission of complex ψ's into Schroedinger's equation does not seem to be a matter *sine qua non;* and since our theory thus far deals only with stationary states, it does not appear that the second difference is vital.

The third difference concerns the fact that our dynamical system is non-conservative (i.e., V contains t); if it were conservative, the right side of Eq. (3.8) would vanish identically and our procedure would become as meaningless as it was in 1926, when Schroedinger[3] went through a similar performance. Two circumstances indicate that this third difference is *not* of primary significance: (a) Our system is assumed to be in a quasi-conservative state in which the energy hovers about a definite value and to which we might, experimentally, ascribe a conservative character; (b) the Schroedinger equation is *not exact.* It requires correction at least for "spin."[3]

Compared with the outstanding equivalence of the two equations in form and meaning, these differences cannot be considered basic. It is submitted that *Schroedinger's equation for stationary states is a consequence of classical physics.*

This violent conflict with accepted theory is emphasized by other conflicts; for instance, Eq. (3.2) which (without the $\pm$ sign) was written by Schroedinger in 1926, has long since been read out of the quantum theory; here it plays a fundamental role as the connection between the probability and action functions. Of greater significance is a conflict concerning the occupation of the discrete stationary states predicted by Eq. (3.10); quantum theory asserts that only these states are occupiable, to the total exclusion of the intermediate continuum of states; our classical derivation, although not yet providing an "occupation" formula, cannot accept this complete exclusivity. It is submitted that there is experimental evidence in favor of non-exclusivity, *viz.*, the overlapping of discrete and continuous spectra.

How, despite these and other conflicts, the two theories may nevertheless reach the same or similar results, can be glimpsed from the simplest example—that of a uniform stream of particles moving with constant momentum. Our theory simply asserts that the probability in this case is constant *a priori;* Eq. (3.10) above is *not applicable* here because its derivation breaks down completely. Quantum theory, however, accepts Eq. (3.10) at its face value for this (as any other) case, takes a complex exponential solution for U, and then washes it out by complex multiplication to get a constant probability.

This example serves also to illustrate the care necessary in handling the theory presented here. To take a more general case, suppose the momentum of the system can be resolved into two components $\mathbf{p}_1=\text{grad } W_1$ and $\mathbf{p}_2=\text{grad } W_2$ such that $\text{div } \mathbf{p}_1\neq 0$, $\text{div } \mathbf{p}_2=0$. Then Eq. (3.5) becomes

$$\nabla\cdot\mathbf{p}_1=\mp 2(\mathbf{p}_1+\mathbf{p}_2)^2/k. \tag{3.11}$$

Putting $W_1=\pm k\log U_1$, the corresponding Schroedinger equation becomes

$$\sum\frac{\partial^2 U_1}{\partial x_i^2}+\frac{1}{k^2}(\mathbf{p}_1^2+4\mathbf{p}_1\cdot\mathbf{p}_2+2\mathbf{p}_2^2)U_1=0. \tag{3.12}$$

Perhaps we may be able to gain from results of

[3] If $V=V_1$ (conservative)$+V_2$ (non-conservative), V_2 can be formally eliminated by taking it over to the right of Eq. (3.8) and minimizing it with $\partial R/\partial t$. This introduces a momentum error like that of Sec. II and increases the "sufficiency" perils.

this kind an understanding, in the classical sense, of the non-classical rules of quantum theory for angular momentum, etc.

IV. ATOMIC DYNAMICS, CONTINUED

The conflict mentioned in Section III between our theory and quantum mechanics concerning the occupancy of intermediate states seems to be irreconcilable—although quantum mechanics appears to have made some preconcession in the form of "weak quantization." The conflict of formalisms, *per se*, is not necessarily irreconcilable, for it is conceivable that some ingenious "frame of reference" may be found which will make the two formalisms agree, insofar as agreement is inherently possible. In any case, the restriction to real U's in Eq. (3.10) is inconvenient, so we present here the results of an attempt to introduce complex U's in the naive way.

If, instead of transforming the action function W by means of Eq. (3.2), complex U's are introduced by writing

$$W=\tfrac{1}{2}k \log UU^*,$$

where

$$U=\rho \exp(i\Theta), \quad U^*=\rho \exp(-i\Theta), \quad (\rho,\ \Theta \text{ real}),$$

and if U and U^* are required to satisfy the same equation for stationary states, then it is found that: (a) U and U^* must be related by

$$U^*\Sigma\frac{\partial^2 U}{\partial x_j^2}=U\Sigma\frac{\partial^2 U^*}{\partial x_j^2}, \tag{4.1}$$

which is equivalent to the following relation between the amplitude ρ and phase Θ:

$$\text{div.}\ (\rho^2 \text{ grad } \Theta)=0. \tag{4.2}$$

(b) The phase Θ must appear explicitly in U as $\exp(i\Theta)$. (c) The equation for stationary states becomes, in place of Eq. (3.10),

$$\Sigma\frac{\partial^2 U}{\partial x_j^2}+\left(\frac{p^2}{k^2}+(\nabla\Theta)^2\right)U=0, \tag{4.3}$$

i.e., the term $(\text{grad } \Theta)^2$ is added.

Equation (4.1) is also equivalent to

$$\Sigma[2(\partial\rho/\partial x_j)(\partial\Theta/\partial x_j)+\rho\partial^2\Theta/\partial x_j^2]=0,$$

so that if $\Sigma\partial^2\Theta/\partial x_j^2$ vanishes, the relation (4.1) implies that grad ρ shall be perpendicular to grad Θ. If, for example, in a 3-dimensional problem in spherical coordinates, $U=u(r,\theta)\exp(im\varphi)$, the resulting "wave equation" is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\frac{\partial u}{\partial\theta}\right)+\frac{p^2}{k^2}u=0, \tag{4.4}$$

in which the term $m^2u/r^2\sin^2\theta$ is cancelled, so that m does not enter the equation at all; this is not surprising since $P=UU^*$ is independent of m and φ in this case.

The concept of "smoothest density" introduced in Section I for purely mathematical cases can be applied equally well to the kinematical probability P. Following the previous pattern, we define the "characteristic" or "smoothest" P, (call it P_c) by the equations

$$(\text{grad log } P)^2-\left(\frac{d}{ds}\log P\right)^2=G^2$$

$$\delta\int G^2P_c\,d\tau=0.$$

Using Eq. (2.8), putting $P_c=U_c^2$, and carrying out the variation, we find the result is

$$\Sigma\frac{\partial^2 U_c}{\partial x_j^2}+\left(\frac{\nabla\cdot\mathbf{p}}{2p}\right)^2U_c=0.$$

Inserting the value of div $\mathbf{p}$ given by Eq. (3.5) this is reduced to Eq. (3.10). Thus the *kinematical probability $P=U_c^2$ defined by the Schroedinger equation (3.10) has the "smoothest" property.*

We conclude with a brief discussion of our "quasi-conservative stationary states." They imply some sort of stabilizing forces which have hitherto been lacking on any theory. It will now be shown by a simple one-dimensional example how this hiatus may be filled by means of an electromagnetic wave field. Consider a particle moving in a field of force determined partly by a conservative potential $V_1(x)$, and for the rest by the potential of a traveling wave field

$$V_2(x,t)=A(x)\sin 2\pi\nu\left(t-\int dx/v(x)+\alpha\right),$$

where $v(x)$ is the phase velocity and α is constant.

The equation of motion is

$$m\ddot{x} = -\partial V_1/\partial x - \partial V_2/\partial x. \quad (4.5)$$

This equation is, in general, completely intractable, but it ceases to be so if the particle travels at or nearly at the phase velocity. We may call this condition "phase-mechanical resonance."

Suppose first that the particle's velocity is exactly equal to that of the phase, i.e., that $\dot{x}=v$. Then $t-\int dx/v$ is a constant which may be put equal to zero. Equation (4.5) now becomes

$$m\ddot{x} = -V_1' - A' \sin\alpha + (2\pi\nu/v)A \cos\alpha. \quad (4.6)$$

Denote the values of x which satisfy Eq. (4.6) by y, and put $x=y+\eta$ where η is supposed so small that only its first power need be retained in the Taylor expansion of all functions involved and in all products of such expansions; also, let v vary sufficiently slowly so that η/v can be written for $\int d\eta/v$. Forming the expression for $m(\ddot{y}+\ddot{\eta})$ obtained under these conditions and using Eq. (4.6), we find the result is

$$m\ddot{\eta} = -\eta(V_1'' + A'' \sin 2\pi\nu\alpha - (4\pi\nu/v)A' \cos 2\pi\nu\alpha - (2\pi\nu/v)^2 A \sin 2\pi\nu\alpha). \quad (4.7)$$

Equation (4.7) shows that if the parenthesis on the right is positive, the particle is stabilized against small displacements from exact "resonance" even if V_1 and A vary slowly or are constant; and Eq. (4.6) shows that under suitable circumstances large interchanges of energy can take place between a wave and a particle in "resonance" with it.

A macroscopic example of this sort of thing is furnished by the cyclotron or Lawrence's linear ion accelerator which preceded the cyclotron. Better examples, I believe, exist in some electronic devices. These examples require more complicated functions for their representation, but otherwise they illustrate the phenomenon of "rectification" which arises when a particle in a wave field "rides with the wave." This concept of phase-mechanical resonance goes further than supplying stabilizing means for electrons in special orbits; it also provides means for understanding such phenomena as electron diffraction in terms of classical physics. Indeed, phase mechanical resonance represents an inversion of *physical* ideas of quantum mechanics corresponding to the inversion of *mathematical* ideas on which this paper is based. Thus, quantum mechanics ascribes the non-classical behavior of electrons to "matter waves" associated with electrons; our theory would put the waves as an "atmosphere" around the nucleus and ascribe to them a classical electromagnetic character. In the quantum case, the speed of the particle is exactly equal to the group velocity of the matter waves; in our case, the speed of a particle in phase-mechanical resonance is equal or nearly equal to the phase velocity of the electromagnetic waves.

To develop these concepts further, one would have to consider stationary waves also, but the situation then becomes obscure on account of trigonometric terms of double frequency which arise. More important, however, is the question of how such wave systems can exist at all, for, according to ordinary classical theory, they would radiate themselves away in short order. For a discussion of this question the reader is referred to my paper on the "Development of electromagnetic theory for non-homogeneous spaces."[4] We may look to an extension of classical theory of the kind there described for the existence and properties of the wave systems here postulated.

[4] B. Liebowitz, Phys. Rev. 64, 294 (1943).

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Comments on Bethe's Theory of Diffraction of Electromagnetic Waves by Small Holes*

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November 3, 1944

IN this interesting paper Professor Bethe develops a vectorial theory of diffraction of plane electromagnetic waves through a circular aperture in an infinite plane conducting screen, for the limiting case when the aperture is small in comparison with the wave-length. In the introduction Professor Bethe points out that if the problem is attacked by Kirchhoff's method one obtains a solution which fails to satisfy the boundary conditions, and this result he designates as a "failure of the Kirchhoff theory." The method adopted by Bethe is to replace the aperture by an equivalent distribution of magnetic currents, for which he obtains an explicit solution satisfying the boundary conditions.

It should be pointed out that Kirchhoff's method consists in making a certain approximation when solving Helmholtz's equation which, as Professor Bethe states, is justified in the limit of short wave-lengths. Kirchhoff was careful to stress the limitation of his method to wave-lengths which are small in comparison with the size of the aperture. When he took up the case of diffraction by a grating he made the following statement: "The equation derived above makes the essential assumption that the dimensions of the aperture are very large in comparison with the wave-length, and its application to diffraction spectra produced by gratings whose lines are only a few wave-lengths wide, is not justified." From this statement it is clear that Kirchhoff considered his approximation to be unjustified in the case where the wave-length is a moderate fraction of the aperture, let alone in the other extreme case, considered by Bethe, where the aperture is very small compared with the wave-length. For this case there is no "Kirchhoff theory," and therefore one cannot speak of a failure of the Kirchhoff theory.

A method of solving Helmholtz's equation in the case of long wave-lengths, when Kirchhoff's approximation cannot be made, was given some fifty years ago by Lord Rayleigh.[1] The problem solved by Rayleigh is scalar, but his method is essentially the one used by Bethe in the more complicated vectorial problem. Rayleigh's results, especially for the pertinent case where the wave function is made to vanish on the screen,[2] agree with Bethe's as far as order of magnitude is concerned. In a later paper[3] Rayleigh extends his method (in the two-dimensional case) to apertures which are of the dimension of a wave-length.

A systematic exposition of the application of the Helmholtz-Kirchhoff theory, including the case of "long" wave-lengths, to the scalar problem will be found in Lamb's *Hydrodynamics*[4] where will also be found a discussion of Rayleigh's paper.[5] The question of the retention of the various terms in Helmholtz's equation which Professor Bethe raises in Section 2 of his paper is taken up on page 500.

* H. A. Bethe, Phys. Rev. 66, 163 (1944).
** On leave of absence from the Massachusetts Institute of Technology.
[1] Lord Rayleigh, *Sci. Papers*, Vol. IV, p. 283.
[2] See reference 1, pp. 286, 287.
[3] Lord Rayleigh, *Sci. Papers*, Vol. VI, p. 11.
[4] Lamb, *Hydrodynamics*, pp. 492–520.
[5] See reference 4, pp. 517, 518.

Double Bragg Reflections of X-Rays in a Single Crystal

C. J. DAVISSON AND F. E. HAWORTH
Bell Telephone Laboratories, Inc., New York, New York
October 6, 1944

WHEN a beam of monochromatic x-rays traverses a crystal in a direction to satisfy the condition for *hkl* reflection, the resultant Bragg beam traverses the same crystal in a direction to satisfy the condition for $\langle hkl\rangle_{hkl}$ reflection. The two beams constitute a symmetrical pair. Radiation is reflected out of the primary beam into the

FIG. 1. Double x-ray reflection in quartz.

Bragg beam, and out of the Bragg beam into the primary beam. There is a continuous interchange of radiation between the two beams with a net flow to the less intense.

In the case in which two Bragg beams are produced simultaneously the two beams interchange radiation, not only with the primary beam, but also, through associated reflections, with one another. If the two reflections are $h_1k_1l_1$ and $h_2k_2l_2$, radiation flows from beam 1 to beam 2 via the reflection $(h_2-h_1)(k_2-k_1)(l_2-l_1)$ and from 2 to 1 via $(h_1-h_2)(k_1-k_2)(l_1-l_2)$. These are the associated reflections.

In the still more special case in which the structure factor of one of the reflections is zero, no radiation flows to this beam from the primary beam directly, but radiation does flow to it indirectly via the other reflection and one of the associated reflections. A doubly-reflected beam appears in the place of the non-existent once-reflected beam. The condition for this occurrence is, to repeat, that the primary beam shall satisfy the Bragg condition for the non-existent reflection, and that it shall, at the same time, satisfy the Bragg condition for some allowed reflection. There is the further requirement that the associated reflection also is allowed.

Evidence of what appears to be the occurrence of forbidden reflections is met with, not infrequently, in electron diffraction patterns, more often in patterns produced by single crystals, but in powder patterns as well. Among the explanations of these anomalies which have been proposed is this one of double reflections.[1] The possibility of double reflections in single crystals has thus long been recognized.

We have succeeded recently in demonstrating double x-ray reflections in quartz: A beam from a copper target tube operated at 24 kv and 25 ma is brought onto an etched z-cut (normal to principal axis) quartz crystal at the Cu$K\alpha$ Bragg angle for the non-existent 00·2 reflection (16° 36′). A film in a semicircular cylindrical holder is set to receive a regularly reflected beam through a 140-degree paper-covered window in the holder's inner wall. The crystal and holder rotate together at a uniform rate about an axis normal to the crystal surface (z axis). The axis of the holder coincides with the axis of rotation, and the primary beam meets the crystal on this axis. Half of the time the crystal is eclipsed by the holder which is receiving the primary beam on its outer wall; the other half, the primary beam, reaches the crystal, and any beam which emerges in the direction of regular reflection, while the window is in opposition, reaches the film. At certain angular positions of the crystal the primary beam satisfies not only the condition for 00·2 reflection but for some other reflection (or reflections) as well. As the rotating crystal passes through these positions, the doubly-reflected beams flash out. Those which reach the film produce a characteristic pattern, an example of which is reproduced in Fig. 1—exposure time 72 hours.

The chief features of the pattern are pairs of strong spots. The members of the pair are separated by a little more than 8 degrees, and the pairs themselves by 60 degrees. These are produced by double reflections of the type $(01\cdot1+0\bar{1}\cdot1)$. The spot midway between the strong pairs is itself a close pair, each member of which is produced by two simultaneous double reflections of the type $(01\cdot3+0\bar{1}\cdot\bar{1})$ and $(01\cdot\bar{1}+0\bar{1}\cdot3)$. The identities of the other spots have not yet been worked out. Most of them will be found to have been produced by the simultaneous double reflections.

The complete circular pattern has 6-fold symmetry about its center, and six 2-fold diametric axes. The number of spots discernible in a 60-degree interval of the original of the pattern here shown is 18, making 108 in the whole pattern. The total number of flashes per complete rotation can be calculated from the density of points in the quartz reciprocal lattice and other considerations—the number is about 700. The intensities of most are below the threshold of the present observations.

The masking effects of the generally scattered radiation from the crystal and of the 00·3 Laue beam from the continuous spectrum are suppressed by shielding and filtering; that of the 00·6 and higher order Laue beams is avoided by limiting the tube voltage to exclude the 00·6 wave-length from the spectrum.

A number of interesting questions present themselves. There is, to mention but one, the question of the phase relation between the two beams produced by simultaneous double reflections. These beams are coherent and superposed, and must therefore interfere.

[1] H. Raether, Zeits. f. Physik **78**, 527 (1932); J. A. Darbyshire and E. R. Cooper, Proc. Roy. Soc. **A152**, 104 (1935).

Enhanced Thermionic Emission

J. B. Johnson
Bell Telephone Laboratories, Incorporated, New York, New York
November 1, 1944[1]

A NEW type of electron emission from oxide-coated thermionic cathodes is disclosed by a method of measuring simultaneous thermionic and secondary emission. In this method the heated oxide target is bombarded by the primary electrons from a gun in which the high voltage electron stream can be turned on by a small auxiliary voltage. The steady collector voltage is first applied so that before the bombardment starts the circuit is in electrical equilibrium. The thermionic current is then read by a d.c. meter. Short-time changes in the current to or from the target are observed on an oscilloscope with an intervening amplifier from which d.c. is excluded. Time as short as 2×10^{-7} sec. can be resolved.

When now the primary bombardment is started the oscilloscope shows at first an abruptly rising flow of electrons from the target, followed by a gradual rise to an equilibrium value many microseconds later. When the bombardment is stopped, the electron current drops abruptly by the same amount as the initial rise, and there then follows a more slowly decreasing current. The bombarding primary current shows none of this behavior but begins and ends sharply.

The initial rise or final drop of current is interpreted as the beginning or end of normal secondary emission of the target. It changes little with temperature and varies in the usual way with the primary voltage. At a primary voltage of 1200 to 1500 volts, the ratio of the maximum value of the secondary current to primary current varies from 3 to 5. The emission which persists after the end of the bombardment can hardly be secondary emission but must be of thermionic origin, and presumably the equal rise of emission during the bombardment is of the same kind. This emission varies with the temperature of the target in about the same way as the steady emission, thus following roughly the Richardson law. It increases with bombarding voltage and current density, and may exceed the steady thermionic current in value. It is undoubtedly an enhanced thermionic emission excited by the electron bombardment.

A natural assumption is that the increased emission is caused by a rise in target temperature caused by the bombardment. The temperature rise of the *surface* of the target may be calculated, and is far too small to explain the effect. One must conclude instead that the bombardment temporarily changes the thermionic activity of the oxide target.

This effect no doubt explains the exponential rise with temperature that has been reported for the secondary emission factor of oxide cathodes.[1]

[1] N. Morgulis and A. Nagorsky, J. Tech. Phys. U.S.S.R. **5**, 848 (1938).

Proceedings of the American Physical Society

Minutes of the Meeting of the New England Section at Providence, October 28, 1944

THE twenty-fourth regular meeting of the New England Section of the American Physical Society was held at Brown University in Providence, Rhode Island, on Saturday, October 28, 1944. At least sixty members were in attendance. The invited papers were as follows:

The British Society for Freedom in Science. P. W. Bridgman, *Harvard University.*

The Applied Mathematics Program at Brown University. Dean R. G. D. Richardson, *Brown University.*

The Electrical Properties of Polarized Metal-Solution Interfaces. David C. Grahame, *Department of Chemistry, Amherst College.*

Some Metallurgical Applications of Radioactive Tracers. John W. Irvine, Jr., *Department of Chemistry, Massachusetts Institute of Technology.*

Continuity in Mathematics and Physics. Morton Masius, *Worcester Polytechnic Institute.*

Abstracts of some of the contributed papers are appended; others will appear in the *American Journal of Physics.*

At the business meeting the following officers were elected for the ensuing year:

Chairman, Morton Masius, *Worcester Polytechnic Institute.*
Vice Chairman, R. B. Lindsay, *Brown University.*
Secretary-Treasurer, Mildred Allen, *Mount Holyoke College.*
Members of Program Committee, V. E. Eaton, *Wesleyan University;* Francis W. Sears, *Massachusetts Institute of Technology.*

Mildred Allen
Secretary-Treasurer

Conversion of Non-Rationalized c.g.s. to Rationalized m.k.s. Units in Electromagnetism. Herbert Jehle, *Harvard University.*—The standard method of converting the numerical values of a physical quantity from one unit to another is the substitution of units whereby a physical quantity is considered as an invariant with respect to change of units, e.g., energy = 37 erg = 37 (10^{-7} joule) = (37.10^{-7}) joule. The conversion of the numerical values of **E, B, H,** and of nearly all other electromagnetic quantities may be performed by such a substitution. With the usual choice of units, however, this conversion procedure breaks down for electrostatic flux and for **D,** because the rationalization of Gauss' law was performed by a change of the physical quantity of **D** by a factor 4π. This of course invalidates the substitution method. The most convenient way to solve this dilemma is to keep consistently to the substitution method for converting units; and to choose the units of electrostatic flux in c.g.s., nonrationalized m.k.s., and rationalized m.k.s., respectively, as: 1 statlorentz = 1 lorentz/$3\cdot10^9$ = 1 coulomb/$4\pi\cdot3\cdot10^9$. This proposed introduction of a new c.g.s. unit, the "statlorentz," does not involve any change of numerical values; and therefore leaves all physical equations untouched, as it is the numerical values only which enter into the equations.

Apparatus for the Production and Measurements of Small Motions. Gordon Ferrie Hull, Jr., *Bell Telephone Laboratories, Inc.* (now at Dartmouth College).—A cantilever bar is described for producing small motions of the order of 10^{-5} cm and greater together with an interferometer for measuring these motions. Two methods of using the interferometer are discussed. The first uses an uninterrupted monochromatic light source in which the interference fringes are observed to be visible and stationary for particular amplitudes of oscillation. The second method uses a stroboscopic light source synchronized with the oscillating bar. Motions of the cantilever bar measured by these two methods are compared with each other and with the theory of the cantilever bar.

Acoustic Intensity Distribution from a Piston Source. A. O. Williams, Jr., and L. W. Labaw, *Brown University.*—The acoustic intensity distribution from a circular piston-like source, earlier treated by several investigators, is evaluated by an approximate method. The velocity potential, expressed in cylindrical coordinates about the beam (and piston) axis, is expanded in powers of r, with coefficients depending on the known intensity variation along the z axis. The first few terms of the series are computed under certain restrictions of wave-length and dimensions, resulting in a simple, reasonably accurate approximation particularly applicable to narrow supersonic beams. The peak of the intensity curve is a parabola of calculable curvature. This expression permits determination of the cone on the surface of which the intensity falls to one-tenth the axial value. Certain data taken in this laboratory with radiometers and microphones (in water at frequencies near 1 megacycle) allow quantitative comparisons. The general agreement is satisfactory, excelling that resulting from two other approximations used earlier. Since the theory discusses point values, while microphone and

radiometer measure average values over an area, corrections to the latter are necessary. Simple corrections are derived and shown to improve the agreement.

Wave Front Determination in a Supersonic Beam. L. W. LABAW, *Brown University.*—An experimental method has been developed by which the loci of equal phase, in a unidirectional high frequency compressional wave beam in liquids, may be accurately determined without recourse to a standing wave pattern. This permits the tracing of wave fronts in the beam at different distances from the supersonic source, furnishing a new tool for the study of elastic wave diffraction in liquids. The electric signal generated by the piezoelectric action of a Rochelle salt microphone which has the phase of the compressional wave in the liquid is modulated by a small electric signal which has the phase of the voltage impressed across the quartz supersonic generator. The sum of these two signals with the proper amplitudes gives a sinusoidal space variation of the root-mean-square value of the high frequency signal generated by the microphone as it is moved in the direction of propagation of the beam. The locus of points of equal phase may thus be found by following a maximum in this sinusoidal space variation as the microphone is moved at right angles to the direction of propagation. This has the advantage over any optical method since it permits the wave front determination in a beam of circular symmetry.

Research on the Origin of Petroleum. CLARK GOODMAN, *Department of Physics, Massachusetts Institute of Technology.*—During the past two years the American Petroleum Institute has sponsored research on the transformation of organic materials into petroleum. Under the general supervision of technical representatives from all of the contributing oil companies, investigations are in progress at the Scripps Institution of Oceanography on the role of micro-organisms, at Pennsylvania State College on allied bacteriological research and on chemical aspects of the problem, and at the Massachusetts Institute of Technology on the effects of terrestrial radioactivity. The objective of this project is to determine the origin or origins of petroleum in the earth. In addition to being of general scientific interest, it is anticipated that this study will improve the methods of exploration for petroleum. The increased demands for new petroleum reserves imposed by a war economy emphasize the need for such improvements.

A Theory of Singing Flames. ARTHUR TABER JONES, *Smith College.*—A gas flame may sing when surrounded by a resonant air tube. Rayleigh's theory assumes standing waves in the gas supply tube, with most rapid efflux of gas approximately a quarter of a period before maximum compression in the air tube. It is now found that flames may sing without standing waves in the gas tube. In such cases any vibration in the air tube causes progressive waves to run backward through the gas tube, so that the phase of maximum efflux of gas is approximately that of minimum pressure in the air tube. The present work makes it likely that when a flame sings there is often a delay of about half a period between greatest rate of efflux and most rapid supply of heat, thus providing the proper phase relationship for maintenance. When the gas tube ends below in a vessel of some size, standing waves are superposed on the running waves, and if the flame is small and hot, like those employed by Sondhauss, the frequencies maintained show gaps that do not occur when the flame is larger.

The Energy Spectrum of the Primary Cosmic Radiation. SHUICHI KUSAKA, *Smith College.*—The experimental results of Millikan, Neher, and Pickering on the energy incident vertically and the total incident energy at different magnetic latitudes in India and in North America are compared with the theoretical calculations based on the geomagnetic theory of Lemaitre and Vallarta. It is found that the agreement between theory and experiment is within the statistical error if the distribution in number of the primaries is taken to be a curve which follows the inverse cube law for high energy and which flattens out on the low energy side at about 6 Bev. Hence this energy distribution is offered as a possible alternative to the discontinuous one suggested by Millikan and his colleagues based on their atom annihilation hypothesis.

The Deflection Sensitivity of Parallel-Wire Lines in Cathode-Ray Oscillographs. H. GUNTHER RUDENBERG, *Cruft Laboratory, Harvard University.*—The deflection angle θ of a cathode-ray beam accelerated by a potential V is shown to be proportional to the linear charge density ρ transverse to the beam on the interior of the electrostatic deflection system, $\theta=\rho/2V\epsilon_0$. The voltage deflection sensitivity depends on the plate-to-plate capacitance c per unit width, $\theta/E=c/2V\epsilon_0$. This includes edge effects and permits a determination of the sensitivity from capacitance measurements or a simple graphical evaluation from the dimensions of the deflection system. The use of parallel-wire lines as a deflection system is suggested, and its deflection sensitivity evaluated. Such lines have low transit time error and are either easily tuned, or can be operated non-resonant with resistive termination.

Proceedings of the American Physical Society

Minutes of the Meeting of the New York State Section at Schenectady, November 11, 1944

THE Fall Meeting of the New York State Section of the American Physical Society was held in the Physics Building, Union College, Schenectady, New York on Saturday, November 11, 1944. This meeting was sponsored jointly by the Section and the New York State Science Teachers Association. The attendance at the sessions numbered over one hundred and fifty. In view of this large attendance the resolutions committee recommended that joint meetings of the section and the Science Teachers Association receive consideration in the planning of future meetings. The following program of invited papers was presented.

Morning Session

Address of Welcome. Dixon Ryan Fox, *President, Union College.*

Physics in the Secondary Schools of New York State. E. L. Manning, *State Education Department.*

Presentation of A.C. Phenomena for High School Students, Demonstrations. P. I. Wold, *Union College.*

Applications of Electrical Contact Resistance, Polarized Light, and Electron Diffraction Techniques to the Study of Aluminum Surfaces for Spot Welding. R. A. Wyant, G. H. Carragan, and K. H. Moore, *Rensselaer Polytechnic Institute.*

Afternoon Session

Business Meeting.

Demonstrations for Physical Optics, Using Very Short Radio Waves. C. L. Andrews, *New York State College for Teachers, and General Electric Company.*

Night Vision. Brian O'Brien, *University of Rochester.*

New York State Aurora and Geomagnetism. C. W. Gartlein, *Cornell University.*

The biennial election of officers of the Section was reported at the afternoon session and is as follows:

	Terms expire
Chairman, P. R. Gleason, *Colgate University*,	1946.
Vice Chairman, J. R. Collins, *Cornell University*,	1946.
Secretary, W. R. Fredrickson, *Syracuse University*,	1946.
Treasurer, G. H. Cameron, *Hamilton College*,	1946.
Members of Executive Committee,	
C. K. Bosworth, *Glens Falls High School*,	1948.
V. H. Reckmeyer, *Agfa Ansco Corporation*,	1948.

The Executive Committee also includes three others whose terms expire in 1946: W. B. Rayton, Bausch and Lomb Optical Company (ex-chairman); P. F. Gaehr, Wells College; and H. P. Gage, Corning Glass Works.

W. R. Fredrickson
Secretary

Proceedings of the American Physical Society

Minutes of the Meeting of the Ohio Section in Conjunction with the A.A.A.S. at Cleveland, September 11–12, 1944

THE American Physical Society was represented at the Cleveland meeting of the American Association for the Advancement of Science by its Ohio Section, which held in conjunction with Sections B and E of the Association the meetings of which the programmes and some abstracts are hereto appended.

LEON E. SMITH
Secretary

Contributed Papers

Equipment and Techniques for Evaporation of Metals. LEONARD O. OLSEN, CHARLES S. SMITH, AND E. C. CRITTENDEN, JR., *Case School of Applied Science.*

The Evaporation of Metals from Crucibles. CHARLES S. SMITH, LEONARD O. OLSEN, AND E. C. CRITTENDEN, JR., *Case School of Applied Science.*

A Convenient Virtual Image Locator for Elementary Optics. PAUL K. TAYLOR, *Department of Physics, Oberlin College.*

The Energy Balance at the Positive Crater of the Carbon Arc. H. G. MACPHERSON, *National Carbon Company.*

Calculation of the Piezoelectric Effect in Ionic Lattices of the Zinc Blende Type. HANS JAFFE, *The Brush Development Company.*

Non-*K*-Electron Capture by Nuclei of Relatively Low Isotopic Number. ELLIOT Q. ADAMS, *General Electric Company.*

Invited Papers

Medical Physics. OTTO GLASSER, *The Cleveland Clinic.*

Biophysics in Modern War and Technology. DETLEV W. BRONK, *The Eldridge Reeves Johnson Foundation, University of Pennsylvania.*

Mathematical Biophysics in Its Relation to Experimental Biology. N. RASHEVSKY, *University of Chicago.*

Invited Papers on Physics in the Metal Industry

Selection and Training of College Students for Industrial Research. A. W. HULL, *General Electric Company.*

The Strength Properties of Metals. GEORGE SACHS, *Case School of Applied Science.*

Recovery Phenomena in Metals of Continuous Casting. N. P. GOSS, *S.O.M. Center.*

Heat Transfer Problems in the Foundry. H. A. SCHWARTZ, *National Malleable and Steel Castings Company.*

Metallurgical Developments in the Production of Steel Castings. CHARLES W. BRIGGS, *Steel Founders' Society of America.*

The Spectroscopic Laboratory on the Furnace Charging Floor. J. T. ROZSA, *Republic Steel Corporation.*

Quartz Symposium

Joint Meeting with Section E (Geology) of the A.A.A.S.

Quartz for Radio Use—1944. ALLYN C. SWINNERTON, *Office of Chief Signal Officer.*

Quartz as a Mineral Resource. ROBERT B. MCCORMICK, *War Production Board.*

Geology of Quartz Deposits Outside of the United States. CARL TOLMAN, *Foreign Economic Administration;* ROBERT D. BUTLER, *Foreign Economic Administration in Brazil;* RICHARD E. STOIBER, *Office of Chief Signal Officer.*

Geological Investigations of United States Quartz Crystal Deposits with Special Reference to Those of Arkansas. A. E. J. ENGEL AND OTHERS, *Department of Interior.*

Frequency Adjustment of Quartz Oscillator-Plates by X-Rays. CLIFFORD FRONDEL, *Reeves Sound Laboratory.*

Twinning in Quartz. CLIFFORD FRONDEL, *Reeves Sound Laboratory.*

The Interlacing of Piezoelectricity with Other Branches of Science. W. G. CADY, *Wesleyan University.*

The Quartz Crystal Unit. R. A. HEISING, *Bell Telephone Laboratories.*

The Aging of Quartz Crystal Plates. VIRGIL E. BOTTOM, *Camp Coles Laboratory.*

X-Ray Studies of Surface Layers of Crystals. ELIZABETH J. ARMSTRONG, *Bell Telephone Laboratories.*

The Continuing Development of Quartz Crystal Units. KARL S. VAN DYKE, *Office of Chief Signal Officer.*

"Crystals Go to War." A thirty-minute sound and color film. This will be exhibited through the courtesy of the Reeves Sound Laboratory, Inc. The motion picture shows the steps in the manufacture of crystal units in the Reeves plant. It is expected this will be the first public showing of a complete revision of the 1943 film of the same title.

Equipment and Techniques for Evaporation of Metals. LEONARD O. OLSEN, CHARLES S. SMITH, AND E. C. CRITTENDEN, JR., *Case School of Applied Science.*—An 18-inch evaporation system has been designed and constructed along fairly standard lines. An externally operated, four-inch vacuum valve between the diffusion pump and the bell jar allows air to be admitted to the bell jar without cooling the diffusion pump. A large number of evaporations have been carried out using close-wound conical baskets and/or helical coils of nickel, iron, chromel, and tungsten, as well as crucibles (described in the following abstract) as the heating elements. Forty metals have been observed for evaporation behavior with as many of the above-mentioned sources as was deemed feasible. The information obtained supplements the excellent work previously reported by Caldwell.[1]

[1] W. C. Caldwell, J. App. Phys. 12, 779 (1941).

The Evaporation of Metals from Crucibles. CHARLES S. SMITH, LEONARD O. OLSEN, AND E. C. CRITTENDEN, JR., *Case School of Applied Science.*—Metals which alloy readily with those metals ordinarily used for filaments cannot be evaporated in large quantities by the conventional methods. A technique for preparing crucibles for use in such cases has been developed. Ten- to 25-mil tungsten wire is close wound into a conical basket and cleaned and stress relieved by flashing in vacuum. The basket is then painted with a suspension of 325 mesh BeO in HCl (Ph = 1). The crucible is air dried and repainted as often as necessary to build up a uniform and continuous coat of BeO bridging the turns of wire. The product is then slowly heated in vacuum to 1000°C by means of the tungsten element. After holding at 1000°C for 15 minutes and cooling the crucible is found to be hard and quite strong. Such crucibles have been made with a 1-cm³ capacity and used at 1750°C for short periods, and at 1550°C for long periods. A water suspension of fine alumina used in the same way is somewhat more convenient than BeO and is excellent for temperatures below 1200°C. Such alumina crucibles have been given repeated use with different metals.

A Convenient Virtual Image Locator for Elementary Optics. PAUL K. TAYLOR, *Oberlin College.*—The instrument locates a virtual optical image with reference to the position of a real image on a ground glass plate, thus avoiding the parallax method which, for the beginning student, is often confusing and inaccurate. It is adaptable to experiments either with lenses or with plane and spherical mirrors. Correct placement is easily and quickly made with re-settings within one millimeter a usual occurrence.

The Energy Balance at the Positive Crater of the Carbon Arc. H. G. MACPHERSON, *National Carbon Company.*—Measurements were made of the electrical energy input to the crater of a low current carbon arc between solid electrodes and of the losses by radiation from the crater surface, by conduction through the electrode, and by evaporation of carbon. For a $\frac{1}{4}$" graphite anode at 10.5 amperes, 24 percent of the energy was radiated from the crater, 10 percent was lost by evaporation of the carbon, and 66 percent was conducted back along the electrode. In the case of a $\frac{1}{16}$" carbon anode at 12 amperes, 36 percent of the energy was dissipated by radiation from the crater, 11 percent by evaporation, and 53 percent by conduction away from the crater. The relationships between the anode voltage drop, the temperature and area of the anode spot, and the physical characteristics of the anode material are discussed in the light of these results.

Calculation of the Piezoelectric Effect in Ionic Lattices of the Zinc Blende Type. HANS JAFFE, *Brush Development Company.*—Except for some early attempts around the year 1900, no derivations of piezoelectric coefficients from atomic data alone have been published. As a first step, the piezoelectric coefficient e_{14} (ratio of piezoelectric polarization to applied shearing strain) is calculated for an ionic crystal of the zinc blende structure type. The assumption is made that the applied shearing strain will leave the distance between nearest neighbor ions unchanged. The relative displacement between positive and negative ions is thereby completely determined and the resultant polarization is $P_x = e_{14} \cdot x_y = ne/a^2 \cdot x_y$, where ne is the charge per ion and a the lattice constant. The assumption is justified as a starting point by the successful use of fixed ionic radii in estimating stability ranges of structure types. For the crystal zinc blende, ZnS ($a = 5.43$A), we find

$e_{14}=1.08$ coulomb/m^2 for $n=2$. From the best experimental value[1] of the piezoelectric compliance, $d_{14}=3.25 \cdot 10^{-12}$ coulomb/newton, and the elastic compliance s_{44}, we find $e_{14}=0.142$ coulomb/meter^2. The polarity of the observed effect agrees with our derivation for the ionic lattice. As a completely covalent structure would lead to the opposite charge distribution, we conclude that the bond in ZnS is somewhat more ionic than covalent.

[1] K. S. Knol, Proc. Amst. Akad. Sci. [1] **35**, 99 (1932).

Non-*K*-Electron Capture by Nuclei of Relatively Low Isotopic Number. ELLIOT Q. ADAMS, *General Electric Company.*—Radioactive transformations in which nuclei of relatively low isotopic number capture an electron are customarily designated as "*K* capture." Based on the table of Hartree and Hartree for the self-consistent field of mercury, it is estimated that only 87.6 percent of the electrons captured by such nuclei of mercury are from the *K* shell, the contribution from the outer shells being, respectively: *L*, 9.6 percent; *M*, 2.1 percent; *N*, 0.5 percent; *O*, 0.1 percent; and *P*, 0.006 percent. Since only *S* electrons have any appreciable probability of being found at the nucleus, the process is more properly called "*S* capture."

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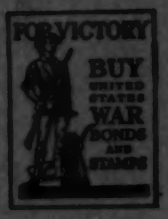

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